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CHEMISTRY OF
COAL UTILIZATION

VOLUME II

PREPARED BY THE COMMITTEE
ON CHEMICAL UTILIZATION OF
COAL, DIVISION OF CHEMISTRY
AND CHEMICAL TECHNOLOGY,
NATIONAL RESEARCH COUNCIL.
. . . . . H. H. LOWRY, CHAIRMAN

PREFACE

At its meeting in November 1937, the Division of Chemistry and Chemical Technology of the National Research Council, recognizing the importance of chemistry to coal technology, voted to organize a Committee on Chemical Utilization of Coal. Subsequently, the following Committee was appointed and given the responsibility of determining what it might accomplish.

Chairman:
H. H. Lowry, Director, Coal Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pa.

Members:
Fred Denig, Vice-President, Koppers Company, Pittsburgh, Pa.
W. S. Landis,* Vice-President, American Cyanamid Company, New York, N. Y.
A. R. Powell, Chief Chemical Engineer, Koppers Company, Pittsburgh, Pa.
F. H. Reed, Chief Chemist, Illinois Geological Survey, Urbana, Ill.
R. P. Russell, Vice-President, Standard Oil Development Company, New York, N. Y.
H. H. Storch, Principal Physical Chemist, U. S. Bureau of Mines, Pittsburgh, Pa.
C. E. Williams, Director, Battelle Memorial Institute, Columbus, O.

Discussion among the Committee members and with other individuals active in scientific and technical aspects of coal utilization led to the decision that the greatest service would be the preparation of a comprehensive, but critical, review of the vast literature that has accumulated on the chemistry of coal utilization. No such review existed in any language. Several books and monographs on special topics were available, most of which, however, treated the work done only in a certain country or by a certain "school" with infrequent reference to other work.

Coal has world-wide distribution, and upon its use depend the industrial welfare and comfort of the greater part of the world's population. As a logical consequence, studies of coal and its utilization have been made throughout the world. Nevertheless, the nature of coal is incompletely understood, and most of coal technology re-

* Deceased.

mains as much an art as a science. A review of the studies already made should serve to put the available data in perspective from which further advances in coal technology should follow.

In all its uses coal undergoes a series of chemical reactions, and, since these are predominantly heterogeneous reactions, the physical as well as the chemical properties of coal are of great importance. Consequently, it seemed essential to include in the review, as relevant subjects, the origin and classification of coals, and the physical properties of coal, together with the chemical nature of coal, and the chemistry of coal carbonization, combustion, gasification, and hydrogenation.

The Committee, having decided on an objective, gave much consideration to its most effective realization. It was clearly recognized that the literature on the chemistry of coal utilization was too extensive for any one person to cover satisfactorily. Accordingly, an outline, presenting 38 separate topics, together with the names of persons qualified to prepare reviews of the topics, was circulated in September 1938 to the members of the Committee for suggestion, modification, and amplification. Full cooperation of each member of the Committee was received, an unusual manifestation of acceptance of the responsibility of committee membership that was deeply appreciated by the Chairman. The replies were collected and a new outline prepared listing all suggested collaborators. The new outline was discussed at a meeting of the Committee in April 1939, and a decision was reached, in the main, on the subjects to form individual chapters in the final review and on the persons to be invited to participate in the work.

An outline of the proposed review was next sent to each of the prospective authors of the individual chapters, and their collaboration was requested. In these negotiations it was pointed out that the review was to cover the literature through 1939 and to be in the hands of the Chairman by July 1, 1940. Suggestions were also solicited for making the review as complete as possible, and several additional chapters were added as a result. The response was extremely gratifying, all requests but one being accepted. However, with the outbreak of war in Europe in 1939 and the consequent increased demands on already busy people, delays in receipt of manuscript were encountered, and the final manuscript was not received until July 1943. Also, certain individuals were unable to fulfill their original commitments, and it became necessary to secure alternates or to add co-authors to complete the manuscripts.

From 1939 to 1942, the following individuals were appointed to the Committee on Chemical Utilization of Coal, in addition to the original membership:

E. P. Barrett, Mellon Institute, Pittsburgh, Pa.
C. C. Boley, Illinois Geological Survey, Urbana, Ill.
R. E. Brewer, U. S. Bureau of Mines, Pittsburgh, Pa.
Gilbert Cady, Illinois Geological Survey, Urbana, Ill.
J. D. Davis, U. S. Bureau of Mines, Pittsburgh, Pa.
A. C. Fieldner, U. S. Bureau of Mines, Washington, D. C.
C. H. Fisher, U. S. Bureau of Agricultural Chemistry and Engineering, Philadelphia, Pa.
A. W. Gauger, Pennsylvania State College, State College, Pa.
W. L. Glowacki, Mellon Institute, Pittsburgh, Pa.
H. A. Gollmar, Koppers Company, Pittsburgh, Pa.
T. A. Hendricks, U. S. Geological Survey, Washington, D. C.
W. H. Hill, Mellon Institute, Pittsburgh, Pa.
L. L. Hirst, U. S. Bureau of Mines, Pittsburgh, Pa.
H. C. Hottel, Massachusetts Institute of Technology, Cambridge, Mass.
H. C. Howard, Coal Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pa.
M. W. Kiebler, Coal Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pa.
W. R. Kirner, Coal Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pa. (National Defense Research Committee, Washington, D. C.*)
M. A. Mayers, Coal Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pa. (Elliott Company, Jeannette, Pa.*)
L. C. McCabe, Illinois Geological Survey, Urbana, Ill. (U. S. Army, Washington, D. C.*)
W. F. McCutcheon, Mellon Institute, Pittsburgh, Pa.
J. J. Morgan, Columbia University, New York, N. Y.
A. A. Orning, Coal Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pa.
E. O. Rhodes, Koppers Company, Pittsburgh, Pa.
H. J. Rose, Mellon Institute, Pittsburgh, Pa. (Bituminous Coal Research, Inc, Pittsburgh, Pa.*)
R. W. Ryan, Consolidated Edison Company, New York, N. Y.
L. D. Schmidt, U S Bureau of Mines, Pittsburgh, Pa.
W. A. Selvig, U. S. Bureau of Mines, Pittsburgh, Pa.
Louis Shnidman, Rochester Gas and Electric Corporation, Rochester, N. Y.
Gilbert Thiessen, Koppers Company, Pittsburgh, Pa.
B. J. C. van der Hoeven. Koppers Company, Pittsburgh, Pa.
J. F. Weiler, Coal Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pa. (Mathieson Alkali Works, Inc., Buffalo, N. Y.*)
P. J. Wilson, Jr, Mellon Institute, Pittsburgh, Pa.
H. F. Yancey, U. S. Bureau of Mines, Seattle, Washington.

* Present address.

In addition to the above membership, M. R. Geer of the U. S. Bureau of Mines, Seattle, Washington, F. H. Gibson, U. S. Bureau of Mines, Pittsburgh, Pa., J. H. Wells, Mellon Institute, Pittsburgh, Pa., and John O'Brochta and Susan E. Woodridge of the Koppers Company, Pittsburgh, Pa., collaborated with the Committee as co-authors of Yancey, Selvig, Wilson, and Rhodes, respectively.

Dr. H. H. Storch was appointed Vice-Chairman of the Committee in December 1940. The Committee membership was decreased late in 1942 to H. H. Lowry, Chairman, H. H. Storch, Vice-Chairman, and A. R. Powell.

Late in 1939, on vote of the membership of the Committee, an Editorial Committee was formed: Fieldner, Lowry (Chairman), Rose, Storch, and Thiessen. This committee met early in 1940 to consider the authors' estimates of the length of their respective chapters, and several revisions in these estimates were suggested. It was decided to submit the manuscript of each chapter as received to two reviewers for criticisms and to return the manuscript to the author with the criticisms. The final responsibility of accepting or rejecting any proposed alteration on the basis of the reviewer's criticism was to be that of the author. This procedure, though most helpful, was discontinued in 1942 in order not to delay unduly the completion of the manuscript. The Editorial Committee decided also that, in literature citations, the author's name should be followed by his initials, that inclusive pages should be given, that the abbreviations should be those used by *Chemical Abstracts* as given in the "List of Periodicals" of November 20, 1936, and in the "Supplement to the List of Periodicals Abstracted" of December 20, 1942, and that references to the patent literature should include the inventor's name and initials, the patent number, and the year of issue. These procedures have been followed as far as possible and have eliminated, in a large measure, copying references from secondary sources where they are generally incomplete and frequently incorrect.

The reviewers of the individual chapters were selected by the Editorial Committee, and grateful acknowledgment of the Committee on Chemical Utilization of Coal is hereby made not only to those of its membership who participated in the review of the manuscripts, but also to the following:

F. M. Becker, U. S. Steel Corporation, Pittsburgh, Pa.
W. T. Brown, Jones & Laughlin Steel Corporation, Pittsburgh, Pa.
H. L. Brunjes, Fuel Engineering Company, New York, N. Y.
A. N. Cole, Carnegie-Illinois Steel Corporation, Gary, Ind.
Gustav Egloff, Universal Oil Products Company, Chicago, Ill.
Abner Eisner, U. S. Bureau of Mines, Pittsburgh, Pa.
P. H. Emmett, Johns Hopkins University, Baltimore, Md.
W. M. Fuchs, Pennsylvania State College, State College, Pa.

R. M. Hardgrove, Babcock & Wilcox Company, New York, N. Y.
H. F. Hebley, Pittsburgh Coal Company, Pittsburgh, Pa.
W. W. Hodge, West Virginia University, Morgantown, W. Va.
I. H. Jones, Koppers Company, Pittsburgh, Pa.
F. W. Jung, Koppers Company, Kearny, N. J.
C. D. King, U. S. Steel Corporation, Pittsburgh, Pa.
A. T. Larson, E. I. duPont de Nemours & Company, Wilmington, Del.
P. V. Martin, Carnegie-Illinois Steel Corporation, Gary, Ind.
D. R. Mitchell, Pennsylvania State College, State College, Pa.
Percy Nicholls,* U. S. Bureau of Mines, Pittsburgh, Pa.
J. H. H. Nicolls, Department of Mines & Resources, Ottawa, Canada.
J. D. Piper, Detroit Edison Company, Detroit, Mich.
H. C. Porter,* Philadelphia, Pa.
O. W. Rees, Illinois Geological Survey, Urbana, Ill.
W. C. Schroeder, U. S. Bureau of Mines, College Park, Md.
J. A. Shaw, Mellon Institute, Pittsburgh, Pa.
R. A. Sherman, Battelle Memorial Institute, Columbus, O.
G. C. Sprunk, U. S. Bureau of Mines, Pittsburgh, Pa.
Edgar Stansfield, Research Council of Alberta, Edmonton, Alberta, Canada.
G. B. Taylor, E. I. duPont de Nemours & Company, Wilmington, Del.
T. E. Warren, Department of Mines and Resources, Ottawa, Canada.
G. R. Yohe, Illinois Geological Survey, Urbana, Ill.

Throughout the period of organization of the Committee and preparation of this report, the interest and help of the Chairmen of the Division of Chemistry and Chemical Technology of the National Research Council, Dr. Herbert R. Moody and Dr. W. Mansfield Clark, and of other officers of the National Research Council have been much appreciated. Since the Division could not provide funds either for preparation of the manuscript and the illustrations for the printer or for the publication of the complete manuscript, negotiations were entered into with three commercial publishers, all of whom showed great interest in the work. A contract for publication of the *Chemistry of Coal Utilization* between the National Research Council and John Wiley & Sons was signed in 1942.

One of the objectives of the Committee has been to make available as widely as possible the knowledge that has been gained from the study of coal and of its utilization. Every effort therefore has been made to keep the price of the report as low as is consistent with maintaining good workmanship. No royalties are to be paid by the publisher either to the National Research Council or to any individual contributor, nor are reprints of the individual chapters to be made available to the authors. The publisher agreed to meet the cost, estimated before the completion of the manuscript, of retyping such parts as might prove necessary to provide the printer with clean copy

* Deceased.

and of redrawing the illustrations for the engraver. These actual costs exceeded the estimate by $1,000 and this excess was covered. by a contribution from the Koppers Company of Pittsburgh, Pennsylvania. This contribution has reduced the price of these volumes by an amount greater than the actual sum involved, and this generous action of the Koppers Company has directly helped the Committee to realize the objective stated in the first sentence of this paragraph.

In a work such as this, with so many collaborators, uniform treatment of the subjects is not to be expected. Each author, who was selected because he was directly engaged in or closely associated with work on the subject of his chapter, was asked not only to discuss its status as disclosed by the literature, but also to point out where additional information would be helpful in advancing knowledge of the subject. The original intention, as previously stated, was to include consideration of all published material through 1939. The manuscripts of many chapters, receipt of which was delayed, included references of papers published in 1942 to 1943. In other chapters, later references were added editorially to those cited in the original manuscript, and, where possible, statistical information was brought up to the latest available at the time of galley proof. Many authors requested permission, which was gratefully granted, to use unpublished data.

Reading of galley and page proof and checking illustrations were done by the Editor, who also prepared the book index, the name index, and the subject index. The book index is a list of all books and monographs referred to in the text, except bulletins, technical papers, and similar serial publications. It was felt that such a list would be of value to all organizations maintaining a library relating to coal and its utilization. The value of a name index has been questioned, but for the many who, like the Editor, associate names with specific information, it has been included. A subject index is always a compromise between completeness and expediency; that included herein was prepared by the Editor with the assistance of the individual authors in most cases.

Though each author is to be regarded as solely responsible for the conclusions drawn in his chapter, the Editor must acknowledge responsibility for many changes which were made primarily in an attempt at uniformity of style. Incomplete or incorrect references were emended by the Editor. Since each author saw only galley proof of his chapter and not the edited manuscript, an indeterminate share of the responsibility for correctness of statement and citation must be acknowledged by the Editor. Care was taken not to change any expression of personal opinion by an author even though the opinion was distinctly contrary to that held by the Editor.

Differences in opinion held on the same subjects by different authors

are evident in many of the chapters where the same experimental data are considered in relation to different topics; they indicate the need for additional facts so that only a unique interpretation is possible. It is this frequent consideration of experimental work in a particular field by more than one author that renders less important the fact that not all of the authors were equally thorough in their reviews of the literature on the subjects of their chapters. Cross references are given in limited number in the text; further cross referencing is available through the subject index.

The Editor's opinion is that a work of this kind might, if the demand appeared, be reprinted, but that a new edition should be unnecessary. *Chemistry of Coal Utilization* should be kept up to date with supplementary monographs on the subjects forming individual chapters or groups of chapters in the present volumes. Errors of omission and commission should be corrected in the supplementary volumes, and it would be greatly appreciated by the Editor if the readers of these volumes would call his attention to errors.

To all those who have contributed so generously to this cooperative work the Committee on Chemical Utilization of Coal acknowledges its gratitude.

H. H. LOWRY
Editor and Chairman of Committee on the Chemical Utilization of Coal, Division of Chemistry and Chemical Technology, National Research Council

COAL RESEARCH LABORATORY
CARNEGIE INSTITUTE OF TECHNOLOGY
PITTSBURGH, PENNSYLVANIA
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CHAPTER PAGE

GAS FROM COAL CARBONIZATION—PREPARATION AND PROPERTIES

ALFRED R. POWELL

Koppers Company, Pittsburgh, Pennsylvania

Coal gas is one of the several products issuing from coal carbonization. In many operations the manufacture of gas is the chief objective, whereas in many others the production of coke is of primary economic interest. The chief object of the present chapter is to outline the most important physical and chemical properties of coal gas, with some description of each of the constituents normally present.

In its present connection the term "coal gas" is used to refer to any gas that results from the carbonization of bituminous or semibituminous coal. In commercial terminology the words "coke-oven gas" and "coal gas" commonly refer to the gas issuing from coke ovens and gas retorts, respectively, but in the present treatment of the subject "coal gas" is used in its broadest sense. Although gas is obtained as one of the products from the carbonization of coal of all ranks, the only commercially important sources are bituminous coal and to some extent semibituminous coal.

Since the theory and practice of gas manufacture have led to a voluminous literature, and since coal-gas manufacture is one of the major branches of this industry, it is obvious that a complete list of references is quite out of the picture. However, many books and reference lists specifically devoted to this subject are available.[1-11]

FORMATION OF COAL GAS

The formation of coal gas during the carbonization of coal is always coincident with the carbonization process itself. When coal is heated out of contact with air to tem-

1 Rittman, W. F., and Whitaker, M. C., *U. S. Bur. Mines, Tech. Paper* **120** (1915), 27 pp.

2 Meade, Alwyne, *Modern Gas Works Practice*, Benn Bros., London, 1921, 815 pp.

3 Davidson, W. B., *Gas Manufacture*, Longmans, Green and Co., London, 1923, 464 pp.

4 Porter, H. C., *Coal Carbonization*, Chemical Catalog Co., New York, 1924, 442 pp.

5 American Gas Association, *Gas Chemists Hand Book*, Third Edition, American Gas Association, New York, 1929, 795 pp.

6 Morgan, J. J., *American Gas Practice*, Vol. 1, Jerome J. Morgan, Maplewood, N. J., 1931, 969 pp.

7 Gluud, W., and Jacobson, D. L., *International Handbook of the By-Product Coke Industry*, Chemical Catalog Co., New York, 1932, 879 pp.

8 Meade, Alwyne, *The New Modern Gasworks Practice*, Vol. 1, Eyre and Spottiswoode, London, 1934, 534 pp.

9 Pacific Coast Gas Association, *Gas Engineers' Handbook*, McGraw-Hill Book Co., New York, 1934, 1017 pp.

10 American Gas Association, *Fuel-Flue Gases*, American Gas Association, New York, 1940, 208 pp.

11 Various reports of Carbonization Committees and Production Committees of American Gas Association, New York. Also various reports of foreign gas associations.

peratures lying below the plastic or soften-
ing range (350 to 400° C), water vapor and
small amounts of gas (largely carbon diox-
ide) are evolved. Important quantities of
gas and other volatile products are not dis-
charged until the temperature of plasticity
of the coal has been reached and exceeded.

The process of heating a coal from ap-
proximately 450 to 600° C and then dis-
continuing the operation constitutes low-
temperature carbonization. Under such
conditions the yield of gas is low, approxi-
mately in the range of 3,000 to 6,000 cubic
feet per ton of coal, although the unit heat-
ing value of this gas is high, owing to a
relatively large content of hydrocarbons
and a relatively small content of hydrogen.
Because of the low yield of gas, low-tem-
perature carbonization is of rather minor
importance in the coal-gas industry as such.

If the heating of the coal is continued to
800° C or higher, the process is then high-
temperature carbonization, and this is the
method used by the coal-gas industry. Un-
der these conditions the gas yield is ap-
proximately in the range of 8,000 to 12,000
cubic feet per ton of coal.

However, high-temperature carboniza-
tion, as applied in the manufacture of coal
gas, is not quite as simple as the above
might indicate. As expressed by Morgan,[6]
"the coal is not distilled at a temperature
but up to a temperature." The gas and
other volatile products from high-tempera-
ture carbonization are therefore not only
those given off in the higher temperature
range but they also include products given
off in the low-temperature range, modified
to some extent by subsequent exposure to
high-temperature conditions while in the
gaseous or vapor state.

The above conditions are true because
coal is heated in a static or unstirred man-
ner in the oven or retort in which it is car-
bonized for the production of gas. As the

heat flows through the walls of the car-
bonizing chamber the layer of coal imme-
diately adjacent to the wall reaches a
rather high state of carbonization before
the heat flows further into the charge to
carbonize more coal. The process thus
continues until the center of the charge of
coal is reached. At any one time the tem-
perature gradients through the carbonizing
chamber are quite sharp, a typical condi-
tion being that the temperature of the fully
coked material near the heating wall will be
about 1,000° C while the uncoked coal in
the center will be about 100° C, or the boil-
ing point of water.

Furthermore, this difference in tempera-
ture is not evenly distributed between the
wall and the center, but is characterized by
an extremely sharp gradient at that layer
in the charge which is just in the process of
being converted from coal into a low-tem-
perature coke. This occurs in the so-called
plastic layer, which is initiated when the
layer of coal has reached a temperature of
about 350 to 400° C and begins to soften
or fuse, and has completed its plastic con-
dition at a somewhat higher temperature
at the time that the plastic mass hardens
and sets. A complete description of this
phenomenon has been given in another
chapter and is also referred to in most of
the books describing the manufacture of
gas.[2, 3, 4, 6, 7]

From the standpoint of gas production
the matter of the path traveled by the
evolved coal gas and other volatile matter
is of more than ordinary importance. Prob-
ably one of the most thorough discussions
of the plastic state of coal in carbonization
including evidence as to the path traveled
by the gas through the charge has been
given by Foxwell.[12]

12 Foxwell, G. E., *Fuel*, **3**, 122-8, 174-9, 206-
10, 227-35 (1924).

Most of the gases and vapors are liberated on the hot side of the plastic zone, that is, the side nearest the heating wall. From there they flow outwards toward the walls and thence pass up through the space between the wall and the coke or between the shrinkage cracks of the coke. A rather minor portion of the gases and vapors pass off on the cooler side of the plastic layer and, choosing the path of least resistance, flow up through the uncoked coal in the center of the charge. Thus the coal gas obtained from the high-temperature carbonization of coal is almost wholly a product that has been subjected to relatively high temperatures despite the fact that much of it is evolved from the coal at rather low temperatures.

The chemistry involved in the carbonization of coal and the evolution of coal gas is extremely complex and cannot be represented by definite chemical equations, largely because the chemical constitution of the coal substance itself is very complex and not determined except in a somewhat general manner. Some years ago Morgan and Soule [13] gave a general explanation of the types of reactions that occur, particularly in the primary stages of the decomposition of coal by heat. An unusually thorough study, including a summary of previous work, was made by Holroyd and Wheeler [14] of the primary thermal decomposition of coal under experimental conditions calculated to eliminate the secondary reactions.

Coal-Gas Ovens and Retorts

Since coal gas is produced from the carbonization of coal and since the commercial equipment for coal carbonization is

[13] Morgan, J. J., and Soule, R. P., *Chem. & Met. Eng.*, **26**, 923-8, 977-81, 1025-30 (1922).
[14] Holroyd, R., and Wheeler, R. V., *Fuel*, **9**, 40-51, 76-93, 104-14 (1930).

described in Chapter 21, the present description is only a résumé of this subject. Details may be found in the chapter referred to above and in various reference books,[2-4, 6-9]

In general, equipment for the production of coal gas may be divided into two classes, based on the size of the chamber for the carbonization of coal. One class uses relatively small chambers, generally referred to as gas retorts. The other class uses much larger chambers and these are referred to as byproduct coke ovens.

Gas retorts are further divided into a classification based on the position of the retorts: horizontal, inclined, or vertical.

The horizontal retort is the oldest form for the production of coal gas and is still in use although displaced very largely by other forms. These retorts vary in length from 8 to about 20 feet and have a shape that is roughly a half-cylinder; from the shape of the cross section they are often called D retorts. The flat portion forms the floor of the retort. They are built up into banks or "benches," and through these benches and around the outside of the retorts flow the hot heating gases in a system of flues. The heating gas is usually producer gas made in "built-in" producers provided in the retort setting itself. Recuperators are generally used in the heating system for purposes of heat economy.

The shorter retorts are commonly provided with a door at only one end, and they are called stopped-end retorts; charging of the coal and discharging of the coke are usually done by hand. Most of the longer retorts have doors at each end and are called through retorts. In addition to hand charging and discharging, several ingenious machines have been devised to perform these operations.

Inclined retorts, as the name indicates, are rather long carbonizing chambers in-

clined at an angle of about 30° with the horizontal. As compared to horizontal retorts, the charging operation is considerably simplified, since the coal need only be poured in at the upper end. Discharge of the coke from the lower end, however, cannot usually be effected by gravity alone, and hand labor is necessary to assist in the operation. These retorts are said to possess many disadvantages, and relatively few have been installed in America and Europe.

Among gas retorts the verticals have become the most popular, especially in America and England. Vertical retorts are classified as either intermittent or continuous, the intermittent carbonizing the coal in batches fed to the retorts periodically and completely discharging the coke for each carbonizing period, whereas the continuous take a slow continuous feed of coal at one end and discharge the coke continuously at the other end.

In either type the retorts are in the form of vertical tubes about 20 or 25 feet long, with a roughly elliptical or rectangular cross section, measuring 5 to 10 feet in the long dimension and 8 to 18 inches in the short dimension. The retorts are erected in groups in settings, and the heating gas passes through flues arranged between the individual retorts. Producer gas, either from built-in or detached producers, is used for heating. Heat economy is secured by recuperators, regenerators, or waste-heat boilers.

In all vertical retorts, charging of coal and discharging of coke are accomplished by gravity. In the intermittents the top door of the retort is opened and the full charge of coal is allowed to flow in, after which the door is closed and carbonization is allowed to proceed to completion. The charge of hot coke is withdrawn from the retort by opening the door at the bottom and allowing the coke to run into a hot car where it is later quenched with water.

In continuous verticals the coal feeds continuously into the top of the retort through a special gas-tight coal valve, and the coke is continuously discharged at the bottom through a "coke extractor" into a receiving hopper where the coke cools and is periodically discharged into a small car.

Morgan [6] has summed up the advantages of the various classes of gas retorts as follows:

Advantages of vertical over horizontal retorts:
1. Less ground area for given capacity.
2. Less labor and better working conditions.
3. Adaptable to steaming (discussed later).
4. No very expensive charging and discharging machinery.

Advantages of horizontal over vertical retorts:
1. Coke has less tendency to jam.
2. Cost of installation is less.
3. Ease of inspection and repairs during operation.
4. No machinery in connection with retort itself.

Advantages of continuous verticals over horizontals or intermittent verticals:
1. Every piece of coal is subjected to same treatment in its passage through retort.
2. Quality of gas is constant.
3. No loss of gas and no smoke nuisance due to opening of retort for charging.
4. Heat in coke is saved.
5. Tar and ammonia yields higher, tar less degraded, and less lampblack, cyanogen, and naphthalene formed.

Advantages of intermittent vertical retorts:
1. No machinery to maintain.
2. Ease of inspection and repairs during operation.
3. Coke superior in quality to that from other forms of gas retorts.

In the second general class of equipment for producing coal gas are byproduct coke ovens, as mentioned earlier. These com-

paratively large carbonizing chambers were originally designed for the production of blast-furnace and foundry coke as the primary product. This is the situation in most cases, but in all countries there has been a tendency to install many coke ovens primarily for the manufacture of city gas, with the coke more or less a secondary product.

The modern full-size byproduct coke oven is approximately 40 feet long, 14 feet high, and 16 inches in width, and has a capacity of about 17 tons of coal per charge.[15] The shape is practically rectangular, with a slight taper towards one end. These ovens are erected in long rows in a "battery" of ovens, with the length of the oven at right angles to the length of the battery. Between each oven chamber and the one adjacent to it are heating flues in which gas is burned to furnish the heat for carbonization of the coal. Regenerators are provided in the base of the battery to secure heat economy.

Coal is charged into the ovens from the top of the battery through removable doors in the oven tops. After carbonization is complete, doors at the two ends of the oven are removed and the red-hot coke is pushed out by means of a long ram. The coke is received in a special car which carries it under a spray of water to be quenched.

Although regenerators are provided for heat economy in the large majority of oven installations, recuperators or waste-heat boilers have sometimes been used, especially in some of the older types. So-called vertical flue ovens, with the heating flues arranged vertically, are in more common use than the horizontal-flue ovens, the construction of which has decreased sharply.

In addition to the regular full-sized byproduct coke ovens, there are some installations of small ovens approximately 14 feet long, 8 feet high, and 12 inches wide, and each oven has a capacity of about 2.5 tons of coal per charge. These ovens are designed for the manufacture of city gas for smaller towns and cities.

Beginning in the late '30's, a few installations have been made of sole-flue ovens.[16] These carbonizing chambers are relatively long and wide but very low, so that they resemble in this respect the ordinary byproduct oven chamber turned over 90° and lying on its side. Heating is carried out only from one face of this chamber, and this is from the bottom. The name of this oven is derived from the sole flues that are arranged below the oven bottom for heating purposes.

Aside from differences in the shape and size of carbonizing chambers, differences in methods for charging the coal and discharging the coke, and differences in applying the heat to the coal charge, the carbonization of coal and the production of coal gas are fundamentally the same procedure wherever carried out. One modification, rather important from the standpoint of coal-gas manufacture, should be mentioned. This is the so-called steaming of retorts.[2, 17] It consists of the introduction of steam into carbonizing chambers during the carbonization process, thereby utilizing some of the sensible heat of the coke to produce some blue water gas and thereby enhance the yield of gas at the expense of the coke yield. This is practiced mainly in vertical retorts and is much more common in England than in America.

[16] Thiessen, G., *Ind. Eng. Chem.*, **29**, 506–13 (1937).

[17] Ward, J. T., *Proc. Am. Gas Assoc.*, **1927**, 1347–91.

[15] Denig, F., *Iron Steel Engr.*, **15**, No. 10, 32–53, 63 (1938).

SEPARATION OF COAL GAS FROM OTHER VOLATILE PRODUCTS IN MANUFACTURE

As the coal gas leaves the carbonizing chamber it is always mixed with condensable materials which must, of course, be removed. It also has associated with it small amounts of gaseous compounds which may or may not be removed from the main body of the coal gas for purposes of recovery of a useful byproduct or to make the gas more suitable for distribution and use as city gas.

The first step in treatment of coal gas after it leaves the retort or oven is always condensation. This is accomplished by cooling the gas, whereby the latent heat of the vapors and the sensible heat of the gas are removed, and the liquid condensables are thereby separated from the coal gas proper.

The major condensable materials present in the gas are water and tar. When the gas is cooled, both of these condense more or less simultaneously and are drawn off together, the liquids separating later by reason of the difference in gravity. Coincident with the condensation of water some of the gaseous constituents that are more or less soluble in water also are removed from the gaseous phase; typical of such constituents are ammonia, hydrogen sulfide, and carbon dioxide.

After the cooling and condensation are completed, some tar usually remains in the gas in the form of a mist or fog. To remove this tar mist the gas must next be subjected to some physical treatment, which may take the form of scrubbing, impingement, electrical precipitation, or other schemes for the removal of dispersoids from gas.

After the complete removal of ordinary condensables from the gas, it may be considered that the preparation of coal gas as

such has been completed. However, certain of the gaseous constituents are usually removed also before the gas is considered suitable for use. It is almost universal practice to treat the gas for removal of its ammonia content, not only to make it more suitable for distribution but also to recover a useful byproduct; ammonia may be removed by water scrubbing or by passing the gas through sulfuric acid. It is also very common practice to remove the hydrogen sulfide from coal gas; its removal is compulsory if the gas is to be distributed for city use. Sometimes naphthalene may be removed from the coal gas to prevent stoppages in the distribution system, and hydrocyanic acid may be removed to produce cyanogen byproducts.

Liquid hydrocarbons, known as "light oil," and consisting of benzene, toluene, xylene, etc., may be scrubbed from the coal gas, where they exist in the form of a vapor, and they may constitute a byproduct of great economic importance. In some coal-gas plants these hydrocarbons are not removed but are left in the gas.

To sum up the matter of separation of the coal gas from other materials and other treatment after leaving the carbonizing chamber, it may be said that this takes place in two general steps, as follows: (1) Removal of condensable materials. It is beyond the scope of the present description to give the details of apparatus and commercial methods for the removal of water vapor and tar from the hot coal gas leaving the retort or oven. (2) Removal of gaseous and vapor constituents from the coal gas.

It should be emphasized that the term "coal gas" as used here and in succeeding chapters refers to the entire mixture of volatile products resulting from the carbonization of coal after the ordinary condensables, water and tar, have been re-

TABLE I

TYPICAL ANALYSES OF COAL GAS

Percent by Volume of Moisture-Free Gas

No.	Source	CO_2	O_2	N_2	CO	H_2	CH_4	Illumi-nants	Specific Gravity	Heating Value Btu per cu ft Gross	Net
1	Horizontal retort	2.4	0.8	11.3	7.4	48.0	27.1	3.0	0.47	542	486
2	Inclined retort	1.7	0.8	8.1	7.3	49.5	29.2	3.4	0.47	599	540
3	Continuous vertical retort	3.0	0.2	4.4	10.9	54.5	24.2	2.8	0.42	532	477
4	Intermittent vertical retort	1.7	0.5	8.2	6.9	49.7	29.9	3.1	0.41	540	482
5	Intermittent verti-cal oven	2.1	0.4	4.4	13.5	51.9	24.3	3.4	0.42	520	466
6	Byproduct coke oven	2.2	0.8	8.1	6.3	46.5	32.1	4.0	0.44	569	509
7	Byproduct coke oven	1.8	0.2	2.0	4.5	57.9	30.3	3.3	0.36	567	505
8	Byproduct coke oven	1.3	0.5	9.6	6.9	50.7	27.6	3.4	0.40	542	486
9	Byproduct coke oven	1.6	0.6	8.4	6.5	51.4	28.4	3.1	0.40	537	480
10	Byproduct coke oven	2.0	0.9	7.0	6.2	53.2	26.7	4.0	0.40	580	523
11	Byproduct coke oven	1.5	0.6	6.2	5.3	57.1	25.9	3.4	0.39	557	499
12	Sole-flue coke oven	4.2	1.0	15.6	14.1	43.5	19.0	2.6	0.54	435	392
13	Low-temperature car-bonization	5.1	0.4	2.1	2.9	16.4	70.9	2.2	0.63	914	838

NOTES ON TABLE I

All the figures in this table refer to *dry gas*, that is, gas that is entirely free of water vapor. This is the usual procedure as far as the percentage chemical composition of gas is concerned. It is more common in commercial practice to express the specific gravity and the heating value of gas (Btu per cubic foot) on the basis of gas at 60° F and a pressure of 30 inches of mercury and saturated with water vapor under these conditions of temperature and pressure. In the table, specific gravity and heating value are expressed on the basis of *dry gas* at 60° F and 30 inches mercury. The values given for heating value in the table would be 1.74 percent lower when expressed on the basis of saturation with water vapor at 60° F and 30 inches mercury.

In all normal coal gas some ethane, C_2H_6, is present in addition to the methane, CH_4. It is most common to combine these constituents on the basis that one mole of ethane is approximately equivalent to two moles of methane, and this procedure has been followed in the table.

In some of the gases tabulated the light oil had been removed before the gas was analyzed. This has the effect of lowering the content of illuminants somewhat, and it also lowers the heating value quite appreciably. This will be discussed later in detail under the subject of specific constituents of coal gas.

Also in some of the analyses, a small percentage of producer gas has been added to the coal gas before the point of gas sampling in the plant. The chief effect of this procedure is to raise the nitrogen content of the gas slightly.

The following notes refer to each specific sample of coal gas by number:

Nos. 1–6. These analyses have been taken from the American Gas Association book, *Fuel-Flue Gases.*[10]

No. 7. Monthly average of send-out gas from a byproduct coke plant. Light oil has been removed from this gas.

Nos. 8–9. Monthly average of send-out gas from byproduct coke plants. Light oil has been removed from and producer gas added to these coal gases.

Nos. 10–11. Monthly averages of send-out gas from byproduct coke plants. At these plants light oil has not been removed.

No. 12. Coal gas made from 100 percent Illinois coal. Average of five samples. See ref. 16.

No. 13. Gas made in experimental retort at temperature of 500° C from Pittsburgh Seam coal.[18]

moved. In other words, it is considered that the mixture of gases and vapors resulting after the completion of the first step outlined above is coal gas, and those operations carried out in the second step are treatments of coal gas as such.

COMPOSITION AND PROPERTIES IN GENERAL

Since coal gas is simply a mixture of gases and vapors, its properties will largely be determined by the nature and amount of these various chemical compounds comprising the mixture. Of primary importance, therefore, is the chemical composition of the gas and the percentage limits between which each compound is present under different conditions of manufacture, etc. Of somewhat secondary importance are the physical properties of the coal gas as such, since these properties are determined almost entirely by the separate components making up the mixture.

A few typical analyses of coal gas from the carbonization of different coals, as taken from the literature and other sources, are shown in Table I. It should be emphasized that these represent for the most part gas produced from various commercial plants. Many conditions may have differed in addition to the type of carbonizing equipment employed to produce the coal gas. The detailed notes following Table I should be consulted for an explanation of some of these variables and for literature references.

The method of expressing analyses of coal gas in Table I, although useful for most commercial purposes, does not give the complete story. For example, the figure for carbon dioxide also includes any other acidic constituents that may have been present in the gas, such as hydrogen sulfide and hydrocyanic acid. As mentioned in the notes following the table, the figure for methane also includes ethane and other

members of the paraffin series of hydrocarbons. The term "illuminants" includes many unsaturated and aromatic hydrocarbons, which are lumped together in one class by this terminology. Also present in coal gas are many compounds that occur in very minute amounts and are determined only for special purposes.

A very few "complete" analyses of coal gas have been made by means of fractional distillation of the gas at extremely low temperatures. In Table II are given the results of such analyses of coke-oven gas both before and after the light-oil scrubbers. These analyses were made by the U. S. Bureau of Mines.[19]

The U. S. Bureau of Mines also made a rather exhaustive study of coal gas resulting from low-temperature carbonization.[20] Table III summarizes the results.

These two examples give some idea of the complexity of the composition of coal gases, especially as regards the presence of many different hydrocarbons. Later, still other components of coal gas that are present in very small amounts will be discussed under specific titles.

For certain purposes of gas utilization it is sometimes of interest to know how the chemical analysis of coal gas varies during the period of carbonization. Several investigations of this subject have been made, and the results of one test conducted in England are given in Table IV.[21] This test was made on a coke oven having a width of 16 inches and a coal charge of 13.4 tons

[18] Fieldner, A. C., and Davis, J D., *U. S. Bur. Mines, Monograph* 5 (1934), 164 pp.

[19] United States Steel Corporation, Chemists' Committee, *Sampling and Analysis of Coal, Coke, and By-products,* Carnegie Steel Co., Pittsburgh, Pa., 3rd ed., 1929, p. 134; Yant, W. P., and Frey, F. E., *Ind. Eng. Chem.,* **19**, 1358–61 (1927).

[20] Frey, F. E., and Yant, W. P., *Ind. Eng. Chem.,* **19**, 21–6, 488–93 (1927).

[21] Saunders, S. W., and Smith, F. Frank, *Gas World,* **98**, Coking Sect., 40–3 (1933).

TABLE II

COMPLETE ANALYSES OF COKE-OVEN GAS FROM KOPPERS OVENS [19]

Component	Percent by Volume of Moisture-Free Gas	
	Unwashed	Debenzolized
Hydrogen sulfide	0.7	0.7
Carbon dioxide	1.7	1.5
Nitrogen	0.9	1.0
Oxygen	0.0	0.0
Hydrogen	56.7	57.2
Carbon monoxide	5.7	5.8
Methane	29.6	29.2
Ethane	1.28	1.35
Ethylene	2.45	2.50
Propylene	0.34	0.29
Propane	0.08	0.11
Butylene	0.16	0.18
Butane	0.02	0.04
Acetylene	0.05	0.05
Light oil	0.65	0.15
Totals	100.33	100.07

on the dry basis. The coking period used was 14 hours. The yields of various by-products during each hour of the coking period were also determined, but only the data on the coal gas are presented. Most significant of the trends in the composition of the coal gas are the decrease in hydrocarbons and the corresponding increase in hydrogen as the carbonization process proceeds to completion.

As stated earlier, coal gas is simply a mixture of various gases and vapors, and therefore the chemical and physical properties will, of course, be determined by these components. It is beyond the scope of the present treatment of the subject of coal gas to go into the subject of the chemical and physical properties of these component substances.

Methods for the sampling and analysis of coal gas are given in some detail in the *Gas Chemists Hand Book* of the American

TABLE III

COMPLETE ANALYSIS OF LOW-TEMPERATURE CARBONIZATION COAL GAS [20]

Constituent	Percent by Volume of Moisture-Free Gas
Carbon dioxide	11.0
Hydrogen sulfide	1.0
Nitrogen	1.1
Oxygen	0.0
Hydrogen	33.5
Carbon monoxide	11.7
Methane	32.4
Ethylene	0.92
Acetylene	0.00
Ethane	3.8
Propylene	0.87
Propane	1.33
unsym-Dimethylethylene	0.21
sym-Dimethylethylene	0.18
Ethylethylene	0.12
1,3-Butadiene	0.002+
n-Butane	0.28
Isobutane	0.09
Light oil, etc. (by difference)	1.498
	100.000

Gas Association; [5] this book also outlines methods for determining the density (specific gravity), the heating value, and the water dew point of coal gas. Some typical figures for the specific gravity and heating value of coal gas have already been given in Table I.

The viscosity of coal gas can be determined directly by various methods or else can be calculated with a fair degree of accuracy from the known viscosity of the individual constituents. A complete discussion of this subject, together with a large number of literature references, is available.[22]

[22] Herning, F., and Zipperer, L., *Gas- u. Wasserfach*, **79**, 49–54, 69–73 (1936).

TABLE IV

Variation of Gas Analyses during Coking Period [21]

Hours after Charging	Percent by Volume of Moisture-Free Gas						Gas Produced cubic feet per hr
	$CO_2(+H_2S,$ etc.)	Illuminants	CO	CH_4	H_2	N_2	
1	1.6	4.6	5.3	34.8	52.0	2.1	11,900
2	1.7	4.4	5.3	33.6	53.4	2.3	10,600
3	1.8	4.0	5.3	32.4	54.8	2.5	13,800
4	1.9	3.6	5.3	31.0	56.0	2.6	13,000
5	2.0	3.2	5.3	30.0	57.2	2.7	13,000
6	2.1	2.6	5.3	28.8	58.4	2.8	13,600
7	2.2	2.2	5.3	27.6	59.5	3.0	14,000
8	2.1	1.8	5.3	26.4	60.6	3.1	13,600
9	1.9	1.4	5.3	25.0	61.8	3.2	13,200
10	1.4	1.0	5.3	22.0	66.0	3.4	14,800
11	0.8	0.4	5.3	16.2	72.0	3.6	9,100
12	0.4	. . .	5.3	11.0	78.0	4.1	. . . . . .
13	0.3	. . .	5.3	5.6	84.0	5.5	. . . . . .

Specific Constituents of Coal Gas

In the literature on coal gas there are many references to the presence of literally hundreds of different constituents. This is easily understood when it is considered that coal gas and coal tar are formed simultaneously in the carbonizing equipment and leave the carbonizing chamber as a single stream of gases and vapors. In the condensation process most of the tar vapor and a substantial portion of the water vapor are condensed and thereby removed from the coal gas. Obviously, the coal gas will retain that proportion of the vapor of the various compounds as determined by the partial pressure of these compounds in the liquid condensates. For this reason, all the hundreds of constituents that are known to be present in coal tar are undoubtedly present in coal gas. However, the actual quantity of many of these coal-tar compounds that will be existent in the gas is so extremely minute and so far beyond the ordinary means of detection that it would be quite impractical and confusing to list them as being present.

The list of compounds in Table V is quite selective, including only those that have actually been identified as being present in coal gas, and that are of more or less importance in purifying the gas or recovering commercially important byproducts from it. The data for preparation of Table V have been gleaned from many sources, including two rather complete lists of some of these compounds in published books.[23] Other literature references will be given later in connection with specific compounds in this list. Table V lists the more important constituents of coal gas according to their chemical classification. Another method of classifying them, and one that is most important from the standpoint of purifying the gas and/or removing from it useful byproducts, is to classify the constituents by their physical properties of vapor pressure and solubility in liquid condensates.

For example, the gas is normally satu-

23 Simmersbach, O., and Schneider, G., *Grundlagen der Kokschemie*, 3rd ed., Julius Springer, Berlin, 1930. 366 pp. Hoffert, W. H., and Claxton, G., *Motor Benzole*, 2nd ed., National Benzole Association, London, 1938, 933 pp.

TABLE V

CONSTITUENTS OF COAL GAS

Class	Compound	Formula	Boiling Point, °C
Elements	Hydrogen	H_2	−253
	Nitrogen	N_2	−196
	Oxygen	O_2	−183
Oxides	Carbon monoxide	CO	−192
	Carbon dioxide	CO_2	−78
	Water	H_2O	100
	Nitric oxide	NO	−151
Paraffin hydrocarbons	Methane	CH_4	−161
	Ethane	C_2H_6	−89
	Propane	C_3H_8	−44
	n-Butane	C_4H_{10}	0
	Isobutane	C_4H_{10}	−10
	Higher paraffins	C_5H_{12} to $C_{10}H_{22}$	10 to 174
Olefin hydrocarbons	Ethylene	C_2H_4	−104
	Propylene	C_3H_6	−45
	n-Butene (butylene)	C_4H_8	−5
	Isobutene	C_4H_8	−6
Acetylene hydrocarbons	Acetylene	C_2H_2	−84
	Allylene	C_3H_4	−27
	Crotonylene	C_4H_6	18
Aromatic hydrocarbons	Benzene	C_6H_6	80
	Toluene	C_7H_8	111
	o-, m-, p-Xylenes	C_8H_{10}	138 to 144
	Ethylbenzene	C_8H_{10}	136
	Propylbenzene	C_9H_{12}	158
	Ethyltoluene	C_9H_{12}	158 to 163
	Pseudocumene	C_9H_{12}	168
	Mesitylene	C_9H_{12}	164
	Hemimellitene	C_9H_{12}	176
	Cymene	$C_{10}H_{14}$	157 to 177
	Durene	$C_{10}H_{14}$	196
	Naphthalene	$C_{10}H_8$	218
	Methylnaphthalene	$C_{11}H_{10}$	243
Miscellaneous unsaturated hydrocarbons	Butadiene	C_4H_6	−5
	Cyclopentadiene	C_5H_6	42
	Styrene	C_8H_8	145
	Indene	C_9H_8	178

TABLE V—*Continued*

CONSTITUENTS OF COAL GAS

Class	Compound	Formula	Boiling Point, °C
Oxygen compounds	Phenol	C_6H_6O	184
	o-, m-, p-Cresols	C_7H_8O	187 to 202
	Xylenols	$C_8H_{10}O$	211 to 225
	Coumarone	C_8H_6O	169
Nitrogen compounds	Ammonia	NH_3	−33
	Hydrocyanic acid	HCN	26
	Acetonitrile	C_2H_3N	80
	Pyridine	C_5H_5N	118
	Picolines	C_6H_7N	135 to 138
	Lutidines	C_7H_9N	143 to 170
Sulfur compounds	Hydrogen sulfide	H_2S	−60
	Carbon disulfide	CS_2	46
	Carbon oxysulfide	COS	−50
	Methyl mercaptan	CH_4S	6
	Ethyl mercaptan	C_2H_6S	36
	Methyl sulfide	C_2H_6S	41
	Ethyl sulfide	$C_4H_{10}S$	91
	Thiophene	C_4H_4S	84

rated with water vapor, and decrease in temperature causes condensation. Certain constituents that are more or less soluble in water are partially removed from the gas by the water condensation. Among the water-soluble compounds are ammonia, carbon dioxide, hydrogen sulfide, hydrocyanic acid, phenol and related compounds, and pyridine and related compounds. All these appear in the so-called ammonia liquor, which is discussed in Chapter 32, but a very substantial proportion of these compounds still remains in the gas after the condensation of water has occurred.

Many of the compounds are quite soluble in tar and other oils and have a low enough vapor pressure to be so absorbed. After tar condensation has taken place, the residues of these compounds remaining in the gas may be absorbed by wash oil for

the recovery of light oil from the gas. Such compounds range from cyclopentadiene and carbon disulfide with boiling points of approximately 40° C up through the entire range of hydrocarbons and other oil-soluble compounds to the highest-boiling constituents in the gas.

Lastly, all those constituents which have boiling points less than 40° C and which are not very soluble in water act as more or less "permanent" gases and appear in the finished coal gas in about the same quantity as in the original gas issuing from the carbonizing chamber, unless some special process has been applied for their removal. They comprise by far the major proportion of the coal gas.

Hydrogen. On a volume basis, hydrogen usually is the major constituent present in coal gas. The quantity ranges from 15

percent in gas from low-temperature carbonization to a high limit of about 60 percent in high-temperature carbonization. Because of the very low specific gravity of hydrogen, only about 2 to 10 percent by weight is present in coal gas.

Hydrogen results very largely from a secondary decomposition in the hotter portions of the carbonizing chamber of certain primary gaseous products of the earlier stages of carbonization. In addition, much of the hydrogen also comes directly from coke as higher temperatures convert the low-temperature coke initially formed into high-temperature coke.

Hydrogen is one of the "permanent" gases present in coal gas, and there are no significant changes in quantity or effects on the various gas-treatment processes caused by it. However, it is of great significance in affecting the physical characteristics of the gas, such as specific gravity, and it plays a very important part in the use of the gas for fuel purposes, since the combustion characteristics of coal gas are affected very markedly by the hydrogen content.

In Europe, coal gas is often used as a source of hydrogen for various chemical syntheses, but it is not much used for this purpose in America.

Nitrogen. The nitrogen of coal gas comes from two entirely different sources: one is the coal itself, since free nitrogen is among the products of thermal decomposition of coal; the second is atmospheric nitrogen that leaks in or is added to the gas as waste flue gas, air, or producer gas.

The nitrogen that comes from the decomposition of the coal is rather minor in amount as compared to the total free nitrogen usually present in coal gas. It will probably average about 1.0 percent by volume of the coal gas but may range from 0.5 to 1.5 percent. The total nitrogen content of gas coals is about 1.4 percent by weight, and various studies have indicated that between 15 and 40 percent of this nitrogen will finally appear as free nitrogen in the coal gas. The remainder of the coal nitrogen stays in the coke or is evolved in the form of ammonia, minor percentages coming out in the tar or appearing in the gas as cyanogen compounds.[4, 6, 24]

The atmospheric nitrogen present in coal gas is quite variable in amount, since it is governed entirely by the accidental or purposeful mixing of air, flue gas, or producer gas with the coal gas. This variation is well illustrated in Table I, where the free nitrogen content of the coal gases listed there ranged from 2.0 to 15.6 percent. Allowing 1.0 percent as the amount coming from the decomposition of the coal, the range of atmospheric nitrogen in these gases would be 1.0 to 14.6 percent. It must be kept in mind that this atmospheric nitrogen present in coal gas is not pure nitrogen but also contains the rare gases that are always associated with nitrogen obtained from the atmosphere.

Aside from the accidental inleakage of free nitrogen into coal gas during its manufacture, nitrogen is often purposely added for various reasons. Among these are (1) the addition of air for the purpose of furnishing oxygen in the gas to assist in removal of hydrogen sulfide by iron oxide, (2) the addition of producer gas to regulate and make uniform the heating value and the specific gravity of the coal gas when distributed for city use. Otherwise free nitrogen has no value or function in coal gas. It is classified as one of the "inerts" since it has no heating value. Like hydrogen it is one of the permanent gases,

24 Short. A., *J. Soc. Chem. Ind.*, **26,** 581–5 (1907) ; Stone, C. H., *Gas Age-Record,* **51,** 241–3 (1923) ; Simmersbach, O., *Stahl u. Eisen,* **34,** 1155 9 (1914).

and it is not affected by nor does it affect the various gas-treatment processes in the manufacturing plant, nor does it affect in any way the distribution of the gas through pipe lines, except as it influences the specific gravity of the coal gas.

Oxygen. Free oxygen is present in coal gas only as a result of inleakage or introduction of air after the gas has left the carbonizing chamber. Under the high temperature and strongly reducing conditions of the coke oven or gas retort it would not be expected that free oxygen could exist, and it does not.

Oxygen is found in coal gas in amounts ranging from 0.1 to 1.0 percent. It is very exceptional indeed to have less than 0.1 percent present, and it is usually considered poor operating practice to have more than 1.0 percent.

As stated in the previous section, it is rather common to add oxygen purposely to gas in the form of air in order to assist in the removal of hydrogen sulfide by the iron oxide method of gas purification. In addition to this voluntary addition of oxygen, there is always some incidental leakage or diffusion of air into the gas stream at the manufacturing plant.

Other than its function of assisting in the purification of the gas in the iron oxide boxes of the gas plant, oxygen serves no useful purpose and may be quite detrimental if present in excessive quantities. Oxygen has zero heating value and, like nitrogen, is classed as one of the inerts.

Probably the most harmful property of oxygen, especially when it is present in amounts exceeding 1.0 percent, is its tendency to promote corrosion of metals in the gas-distribution system. The constituents of gas that are the most generally regarded as contributing to corrosion of the interior of gas-distribution systems are oxygen, water, carbon dioxide, hydrocyanic acid, hydrogen sulfide, organic sulfur compounds, and ammonia. Several years ago a bibliography and summary of the subject of corrosion by gas was prepared.[25]

The gas constituent that is probably the most active in causing corrosion is oxygen. This is shown by the fact that iron oxide is the chief material present in corrosion deposits on iron or steel and also by the fact that natural gas under high pressure may produce decided corrosion when the other constituents mentioned above are absent but when a small percentage of oxygen is present.[26]

Another deleterious effect of oxygen in coal gas is in connection with the formation of nitrogenous or "vapor-phase" gum. This will be more properly discussed later under the subject of nitric oxide in coal gas.

Carbon Monoxide. Carbon monoxide is present as one of the major constituents in all commercial coal gas, since it is one of the products resulting from the thermal decomposition of coal. The usual quantity is 6 or 7 percent by volume of the coal gas, but the amount may vary between the limits of 4 and 10 percent. If more than 10 percent carbon monoxide is found in coal gas, the chances are that steaming of the charge has been practiced.

Like the three constituents described previously, carbon monoxide is one of the permanent gases present in coal gas, and it is not affected by the gas-treatment processes in the manufacturing plant. On a volume basis it has about the same heating value as hydrogen, and its effect on the combustion characteristics of the gas is significant.

As is well known, carbon monoxide is extremely toxic when present in air in suffi-

25 Goldsteen, H. A., *Proc. Am. Gas Assoc.*, **1928**, 1258–61.
26 Allyne, A. B., *Gas Age-Record*, **70**, 267 8 (1932).

ciently high concentrations, and for this reason the mixing of comparatively large volumes of coal gas with the air in a room or building may cause fatalities. Since coal gas has a distinctive odor, its presence can usually be detected in advance of a dangerous concentration of carbon monoxide. A selected but quite complete bibliography on carbon monoxide poisoning and its treatments has been prepared.[10]

Carbon Dioxide. Carbon dioxide occurs in coal gas in amounts usually between 1.5 and 2.0 percent by volume. If the content is much higher than 2.0 percent the indications are that flue gas has been mixed with the gas in the carbonizing chamber or possibly that the charge has been subjected to steaming.

Along with nitrogen and oxygen, the carbon dioxide is an "inert" since it contributes nothing to the heating value of the gas. From the standpoint of gas-plant operation the most important property of carbon dioxide is its solubility in water and its tendency to react with ammonia. Therefore, when condensation occurs in the gas-treatment system, not only does a portion of the ammonia leave the gaseous phase along with the condensed water, but also some of the carbon dioxide is dissolved, more or less loosely combined with the ammonia.

As stated previously, carbon dioxide is considered one of the corrosive constituents of gas, owing to its weakly acidic nature. In all probability, however, its corrosive action on the metal of the distribution system is quite mild compared to that of some other constituents present in coal gas.

Water Vapor. Although water vapor is quite often omitted from a list of those constituents found in coal gas, it is of considerable importance from the standpoints both of gas treatment at the plant and of distribution of the gas through mains.

Water is one of the products of the process of coal carbonization, coming both from the free moisture present in the coal and from the "combined water" or water of decomposition of the coal. Most of this water is condensed as ammonia liquor. After the gas has passed through the various treatment processes in the plant, it is usually saturated with water vapor, so that the content of water vapor in the gas is largely determined by the temperature. For example, saturated gas at 60° F would contain 1.74 percent by volume of water vapor, at 80° F it would contain 3.45 percent, etc. Under some other conditions the gas is unsaturated, so that the water content of coal gas must be considered as quite variable and entirely unrelated to the coal used or to the conditions of carbonization.

Water vapor as such is simply an inert and has no significant effect on the distribution of gas or its combustion, except as it may affect the flame temperature. However, the fact that it is a condensable vapor has an important bearing on the distribution of gas. After the coal gas leaves the point of manufacture, any decrease in temperature will cause condensation, if the gas is saturated.

The condensation of water in gas mains, services, and meters often leads to deposits that will cause stoppage of gas flow in mains or customer appliances. One example of this occurs in freeze-ups in exposed sections of pipe, where the condensed water is converted into ice. However, the most universal and harmful effect of condensed water is its action in promoting corrosion of mains; such corrosion may cause stoppages right at the point of formation, or during seasons when the main is dry it may lead to the pick-up by the gas of rusty dust which may then be carried on to cause stoppage of consumers' appliances, etc.

Within recent years the harmful effects due to liquid water condensing from gas into the gas-distribution system have been seriously recognized, and commercial processes have been developed and applied for partial removal of water vapor from gas; these processes have been included under the general designation of "gas conditioning." Most of the important references to moisture in gas and methods for partial removal of moisture have been given by Oppermann in a bibliography on gas conditioning.[27] In 1939, Shively described the latest developments in gas conditioning.[28] These processes have been summarized in Chapter 29.

Nitric Oxide. Only comparatively recently has nitric oxide, NO, been seriously considered as a constituent of coal gas and other manufactured gas. This is not surprising when it is realized that the amount present seldom exceeds 0.0005 percent by volume. A typical figure for nitric oxide content of coal gas is one-hundredth of that just mentioned, or 0.000005 percent (0.05 part per million). The usual range of concentration is from zero to 0.0001 percent (1.0 part per million).

Despite the extremely minute amount present in coal gas, nitric oxide is a constituent of considerable significance since its presence may lead to serious disturbances in customers' gas appliances. The chemical interaction of three gaseous constituents—namely, nitric oxide, oxygen, and certain unsaturated hydrocarbons—leads to the formation in the gas of nitrogenous or "vapor-phase" gum. The reaction proceeds rather slowly under ordinary conditions, and it is only after the gas has attained an age of possibly an hour or more that an appreciable quantity of the nitrogenous

gum makes its appearance in the gas. Even then, the actual quantity produced is extremely minute, and it would never have developed into a trouble-making substance except for the fact that it is present as a very fine fog or mist which remains suspended in the gas stream very persistently. When the gas containing this fine mist of gummy particles passes through a small orifice or is subjected to a sudden change of direction at rather high velocity, many of the gum particles are deposited and in time the deposits lead to a stoppage.

This type of deposit began to be recognized only when range lighters, pilot lights, and various automatic gas appliances that included an orifice or extremely small passage for gas were installed extensively in the homes of consumers. A characteristic of this material is that it affects only equipment of the type mentioned above; it is present in the gas in far too small a quantity to cause stoppage of mains or service lines.

As yet it has not been definitely proved that nitric oxide is one of the products of coal carbonization, although it well may be. At any rate, the major part of the nitric oxide found in coal gas comes from inleakage of flue gas and from combustion gas formed when air is drawn into the carbonizing chamber during periods of charging and discharging. In other words, most of the nitric oxide has the same source as the major part of the nitrogen found in coal gas. It is a well-known fact that one of the minor combustion products resulting from the burning of gas, especially when the flame temperature is high, is nitric oxide, so that inleakage of combustion gas for any reason at all will carry some nitric oxide into the coal gas. An obvious method for decreasing the nitric oxide content of coal gas is, therefore, to prevent as much as possible inleakage of

27 Oppermann, R. H., *Proc. Am. Gas Assoc.,* **1937,** 693–4.
28 Shively, W. L., *ibid.,* **1939,** 501–15.

flue gas and air to the carbonizing chamber.

The literature on nitric oxide in coal gas and other manufactured gas during the last ten years or more has been most extensive. This literature covers the reactions of nitric oxide to form nitrogenous gum, properties of the gum, methods for the analytical determination of nitric oxide in gas, and descriptions of various processes to remove nitric oxide or otherwise counteract its tendency to form gum. Only a few selected references are given here.[29, 30]

Methane and Other Paraffin Hydrocarbons. Next to hydrogen, methane is the most abundant constituent of coal gas on a volume percentage basis. In commercial coal gas the usual amount present lies between 25 and 30 percent by volume, or slightly below or above this range.

From a heating-value standpoint, the methane is by far the most valuable component of the gas since approximately one-half of the heating value of coal gas is contributed by this constituent. It is evident that the combustion properties of coal gas are markedly affected by the presence of the methane.

When coal is carbonized at low temperatures, the methane content of the gas is higher than in gas from commercial high-temperature carbonization. In fact, when the carbonization temperature is quite low, such as 500° C, the volume percentage of methane in the gas may be considerably higher than the percentage of hydrogen. As pointed out earlier, this is because methane is one of the primary products of distillation of coal. When the primary coal gas passes through hot coke and over hot heating walls, as it does in ordinary high-temperature carbonization, a portion of the methane is decomposed into hydrogen, thereby decreasing the methane content and increasing the content of hydrogen.

Methane is a so-called permanent gas and is insoluble and nonreactive throughout the gas-treatment system of the plant, and therefore has no significance from this standpoint.

The second member of the paraffin hydrocarbon series, ethane, is also a constituent of coal gas, but it is always present in much smaller quantities than methane. As indicated earlier, it is very common practice in gas analysis not to determine the ethane separately but to include it with the methane on the basis of one mole of ethane being the equivalent of two moles of methane; this practice, of course, is not strictly correct, but for all practical purposes the error is so slight that it may be neglected. In ordinary high-temperature coal gas the ethane content is usually between 1.0 and 2.0 percent by volume. Under low temperatures of carbonization the ethane content is much higher, varying from 3.0 percent in the higher temperature range to as much as 15 percent when the carbonization temperature is as low as 500° C.

Like methane, ethane is one of the primary products of coal distillation, and its reactions in the hotter zones of the carbonizing chamber are quite similar to those of methane. In respect to its nonreactivity

29 Schuftan, P., *Von den Kohlen und den Mineralölen,* Verlag Chemie, Berlin, Vol. I, pp. 198, 205–8, 1928 ; *Beitrage zur Kenntnis der Kohle,* Verlag Chemie, Berlin, Vol. II, pp. 31–40, 1929 ; *Z. angew. Chem.,* **42,** 757–60 (1929). Jordan, C. W., Ward, A. L., and Fulweller, W. H., *Ind. Eng. Chem.,* **26,** 947–55, 1028–38 (1934), **27,** 1180–90 (1935). Shively, W. L., and Harlow, E. V., *Am. Gas Assoc., Production Conf. (1936)* ; *Trans. Electrochem. Soc.,* **69** (1936), 20 pp. (preprint). Hollings, H., *Inst. Gas Engrs., Commun.* **147** (1936), 59 pp.; *Gas J.,* **216,** 459–68 (1936)

30 Ward, A. L., Jordan, C. W., and Fulweller, W. H., *Ind. Eng. Chem.,* **24,** 969–77 (1932).

throughout the gas-treatment system, ethane resembles methane.

The paraffin hydrocarbons above ethane are found in coal gas, but the quantities present become less and less as the series increases. Propane and the butanes are very seldom determined as such, and then only by some low-temperature fractional distillation method. Reference to Table II shows that propane occurs to the extent of about 0.1 percent and the butanes about 0.03 percent by volume in coke-oven gas. The low-temperature-carbonization gas in Table III shows much higher percentages: 1.33 percent of propane, 0.28 percent normal butane, and 0.09 percent isobutane. Owing to the low content and the absence of any significant effect on gas treatment, distribution, or use, propane and the butanes are of only academic interest in commercial coal gas.

Paraffin hydrocarbons above the butanes, say from pentane, C_5H_{12}, up to decane, $C_{10}H_{22}$, are known to exist in coal gas, but no systematic study has ever been made of the actual quantities of each hydrocarbon present. That these higher paraffin hydrocarbons occur in coal gas is shown by the fact that nearly all of them have been identified as constituents of coal tar.[31]

The practical importance of the higher paraffin hydrocarbons in coal gas arises from the fact that they are absorbed from the gas along with the aromatic hydrocarbons in the recovery of light oil. In the separation of pure benzene, toluene, xylenes, etc., by distillation, the paraffins distil over in the same boiling ranges and thereby contaminate the pure light-oil products. This subject is discussed in more detail in the chapter on light-oil recovery from coal gas.

An approximation of the quantity of higher paraffins in coal gas can be obtained from the paraffin content of light-oil fractions. However, considerable care must be used in interpreting these figures, since the wash oil used for the absorption of the light oil is itself a heavy paraffin oil (at least in America) and some of this wash oil distils over with the recovered crude light oil absorbed from the gas. Application of this approximate method to average figures for paraffin content of light oil indicates that coal gas from ordinary high-temperature carbonization contains about 0.01 percent by volume of the higher paraffin hydrocarbons.

Ethylene and Other Olefin Hydrocarbons. In the ordinary system of gas analysis, this series of hydrocarbons is included in the "illuminants" along with aromatic hydrocarbons, etc. Separate determination of the various olefin hydrocarbons is therefore obtained only by special methods, such as low-temperature distillation.

Ethylene, C_2H_4, is the most abundant of the olefins in coal gas. Table II shows that the quantity in that particular sample of coke-oven gas was 2.50 percent—probably a typical average figure. Ethylene in coal gas is rapidly decomposed into methane and carbon at temperatures above 600° C, and this may be catalyzed by iron oxide, etc.[12] However, in coal-gas retorts and ovens the gas is removed rapidly enough from the hot zone and cooled below this temperature to prevent attainment of equilibrium at the higher temperature.[32]

Although the amount of ethylene in coal gas is not large, this constituent contributes appreciably to the heating value since its heat of combustion on a volume basis is quite high. Since ethylene burns with a

31 Lunge, G., *Coal Tar and Ammonia*, 5th ed., D. Van Nostrand Co., New York, 1916, Part I (Coal Tar), pp. 207–11.

32 Brooks, B. T., *The Non Benzenoid Hydrocarbons*, Chemical Catalog Co., New York, 1922, p. 33.

very luminous flame, it is one of those compounds in gas that makes the coal-gas flame luminous when primary air is not added to the gas before the burner, and therefore it is included in the group of compounds called "illuminants."

In coal-gas manufacture, ethylene is one of the permanent gases and has no effect on, nor is it affected by, the treatment processes in the plant. Mention will be made in another chapter of special processes that have been proposed or used for the removal of ethylene from coal gas, thereby converting it into ethanol or other useful products.

The second member of the olefin series, propylene or propene, C_3H_6, also occurs in coal gas but in considerably smaller amounts than ethylene. An average figure for commercial coal gas is about 0.3 percent.

The butylenes or butenes, C_4H_8, are found in coal gas, but, as would be expected, the quantities are even less than for propylene. The figure of 0.18 percent given in Table II is probably typical.

Acetylene Hydrocarbons. Some of the lower members of this series of hydrocarbons are present in coal gas from high-temperature carbonization but apparently are absent in coal gas made at lower temperatures. The coke-oven gas shown in Table II contained 0.05 percent of acetylene, and probably allylene and crotonylene were also present but in such minute quantities that they could not be detected. Harzer[33] claimed that in addition to acetylene, C_2H_2, he had detected in coal gas not only allylene, C_3H_4, and crotonylene, C_4H_6, but also various other higher members of the acetylene series. He gave no quantitative results. In the ordinary method of gas analysis, acetylene and its derivatives are included in the "illuminants."

[33] Harzer, A., *J. Gasbeleucht.*, **57**, 622 (1914).

Because of the very small amounts present, and the lack of any significant reactions in the treatment of gas, acetylene is considered one of the minor constituents. Years ago, when the candle-power standard for gas was in effect, acetylene undoubtedly contributed to a significant extent to the luminous quality of the flame, but the candle-power standard has now been almost completely replaced by the heating-value standard.

Aromatic Hydrocarbons. The aromatic hydrocarbons, and particularly benzene and its homologs, are among the most important constituents of coal gas. Although collectively they comprise 1 percent or less by volume of the coal gas, they account for about 5 percent of the heating value.

However, the economic importance of these hydrocarbons does not depend primarily on their contribution to the heating value of the gas, but does become of great significance when the vapors are scrubbed out of the gas to recover "light oil." Since the recovery of light oil is one of the most important treatments to which coal gas is subjected, Chapter 28 of this book is devoted to the subject. For this reason, the present description of the aromatic hydrocarbons will be very sketchy, and reference should be made to the chapter on light oils for more detailed information.

It should be pointed out that, although all the aromatic hydrocarbons in coal gas come out in the light oil in a more or less complete condition of recovery, light oil is not completely composed of aromatics. However, since an average light oil will contain approximately 85 percent of aromatic hydrocarbons, it provides a good basis on which to estimate the amount of the various hydrocarbons present in coal gas.

The yield and composition of light oil vary over a wide range, depending mostly

on carbonizing conditions. The composition and yield of crude light oil from coke-oven gas shown in Table VI is quite typical of many plants.[4]

TABLE VI

COMPOSITION AND YIELD OF LIGHT OIL [4]

Component	Yield, gallons per ton of coal
Pure benzene	1.85
Pure toluene	0.45
Xylenes and light solvent naphtha	0.30
Unsaturated hydrocarbons, etc.	0.16
Heavy hydrocarbons and naphthalene	0.24
Wash oil	0.20
Total crude light oil	3.20

Benzene is the most abundant of the aromatics in coal gas. If the figure in Table VI is considered to represent 90 percent of the benzene in the gas (the remaining 10 percent passing on with the debenzolized gas) and the gas yield is considered as 11,000 cubic feet per ton of coal, the percentage by volume of benzene vapor in the coal gas is 0.66. On the same basis toluene vapor is present to the extent of 0.13 percent by volume. The yield of pure xylenes averages about 0.20 gallon per ton of coal under commercial conditions. The content of xylene vapor in coal gas is therefore about 0.05 percent by volume.

No satisfactory quantitative study has ever been made of the benzene-ring hydrocarbons heavier than the xylenes. They are included, along with other types of compounds, in the commercial fractions of light oil known as "light solvent naphtha" and "heavy solvent naphtha." The combined quantity of these hydrocarbons recovered is approximately 0.20 gallon per ton of coal; or about 0.05 percent by vol-

ume of the vapors is present in coal gas made in normal commercial practice.

Naphthalene and its homologs are present in coal gas that has been subjected to average condensation conditions in an amount equal to about 0.02 percent by volume. This refers, of course, to normal high-temperature carbonization of coal, as do all the estimated figures given above. In low-temperature-carbonization gas, naphthalene is absent. The presence of naphthalene in coal gas is of considerable significance in connection with coal-gas manufacture and distribution, since it is a solid material that easily condenses in gas pipe-lines, causing stoppages.

Table VII summarizes the typical average quantities of the aromatic hydrocar-

TABLE VII

AMOUNTS OF AROMATIC HYDROCARBONS IN COAL GAS

Component	Percent by Volume in Coal Gas
Benzene	0.66
Toluene	0.13
Xylenes	0.05
Ethylbenzene	
Propylbenzene	
Ethyltoluene	
Pseudocumene	0.05
Mesitylene	
Hemimellitene	
Cymene	
Durene	
Naphthalene } Methylnaphthalenes }	0.02
Total aromatic hydrocarbons	0.91

bons present in normal coal gas. In the ordinary methods of gas analysis, the aromatic hydrocarbons are included in the "illuminants."

Miscellaneous Unsaturated Hydrocarbons. Although there are undoubtedly an

extremely large number of unsaturated hydrocarbons in coal gas, only four, other than the members of the olefin and acetylene series, are important enough to deserve mention. They are butadiene, cyclopentadiene, styrene, and indene. All are included in the "illuminants" in the ordinary methods of gas analysis.

Some tests made in England on the butadiene content of coal gas from horizontal retorts and coke ovens indicate the presence of 0.005 to 0.01 percent by volume.[34] Some unpublished results obtained from coke-oven gas in this country have shown 0.02 percent by volume. Probably the only fact of any great importance regarding the presence of this hydrocarbon is its tendency, in common with other conjugated dienes, to react with nitric oxide and oxygen to form nitrogenous or "vapor-phase" gum in gas distribution systems (see nitric oxide, page 936). Because of its high vapor pressure, butadiene is not recovered with the light oil to any appreciable extent.

Cyclopentadiene, on the other hand, has a vapor pressure sufficiently low to cause its partial removal from coal gas in the recovery of light oil. Since its boiling point is 42° C, the cyclopentadiene comes over in the "forerunnings" fraction in the distillation of crude light oil. After recovery in the form of a liquid, the cyclopentadiene, C_5H_6, has a pronounced tendency to polymerize to the dimer, dicyclopentadiene, $C_{10}H_{12}$. This is discussed in more detail in the chapter on recovery of light oil from coal gas. (See Chapter 28.) •

Some tests of crude light oil in France showed the recovery of 15 to 20 kilograms of cyclopentadiene (dimer) from 300,000

cubic meters of coke-oven gas,[35] equivalent to about 0.002 percent by volume in the gas. Some unpublished results obtained from coke-oven gas in this country have shown recovery equivalent to about 0.004 percent by volume in the gas. Assuming that one-half of this hydrocarbon in the gas is recovered along with the light oil, the cyclopentadiene content of coal gas may be estimated at 0.006 percent by volume.

Like butadiene, the cyclopentadiene may enter into the formation of nitrogenous gum in gas-distribution systems. Another significant fact concerning cyclopentadiene is that it may be recovered from the light-oil forerunnings as a useful byproduct of coal carbonization.

Styrene and indene are two hydrocarbons that can be discussed more or less together since they are quite similar in certain behaviors that make them of interest to the gas industry. Both are liquids, styrene boiling at 145° C and indene at 178° C. They are more or less completely removed from coal gas in the recovery of light oil. On distillation of the light oil, styrene appears chiefly in the light solvent naphtha fraction and indene in the heavy solvent naphtha.

The presence of these hydrocarbons in manufactured gas first attracted attention by their tendency to polymerize and form "liquid-phase" gum in distribution systems, when they condensed from the gas as "drip oil" or condensate.[36] However, this trouble is confined almost entirely to carburetted water gas, since coal gas is relatively dry as far as condensation of oil is concerned.

[34] Gooderham, W. J., *J. Soc. Chem. Ind.*, **56**, 26–36T (1937).

[35] Horclois, R., *Chimie & Industrie*, Special No., 357–63, April, 1934.

[36] Brown, R. L., *Proc. Am. Gas Assoc.*, **1924**, 1353–411.

The chief importance of these hydrocarbons in coal gas lies in their usefulness as byproducts. When the proper light-oil fractions containing them are subjected to a catalyst, generally concentrated sulfuric acid, rapid polymerization takes place, and, after the unpolymerized hydrocarbons are distilled off, resinous substances remain.[37] The styrene and indene resins, together with coumarone resins mentioned later, constitute important commercial materials. Furthermore, these hydrocarbons, especially styrene, are used in combination with other substances to make many of the modern types of synthetic plastics.

Tests on coal gas from various sources show styrene contents ranging from 0.002 to 0.006 percent by volume, and indene contents ranging from 0.004 to 0.013 percent by volume.[30]

Oxygen Compounds. In Table V, several organic oxygen compounds are listed as being present in coal gas. The first three, phenol, cresols, and xylenols, are homologs of one another and are often referred to jointly as "tar acids." The fourth compound, coumarone, has nothing in common with the tar acids, other than the fact that it happens to be an organic oxygen compound. Phenol, the cresols, and the xylenols have little significance as constituents of coal gas proper. On the other hand, they are very important constituents of coal tar and also of the ammonia liquor condensed from hot coal gas, and they are discussed in some detail in chapters dealing with those subjects.

Since the tar acids have very low vapor pressure and are quite soluble in tar oils and also in water, they are removed from the gaseous phase very rapidly during condensation and cooling of the coal gas.

Some unpublished tests on coke-oven gas show 0.006 percent by volume of tar acids present in the gas before the final coolers; after the direct final coolers, the content of tar acids in the gas was only 0.0004 percent by volume.

Coumarone is usually discussed in connection with styrene and indene, since it possesses similar properties of forming resins or gums. Like styrene and indene, coumarone is largely removed from the gas along with the light oil and appears in the solvent naphtha fraction on distillation. Resins are produced from coumarone in much the same manner as from styrene and indene.[37] Very little information is available on the quantity of coumarone present in coal gas before removal of the light oil, but it is about of the same order of magnitude as the styrene and indene content.

Nitrogen Compounds. By far the most important nitrogen compound of coal gas is ammonia. Hydrocyanic acid is also of considerable interest. Several organic compounds of nitrogen are likewise present in coal gas, although they are of rather secondary importance from the standpoint of gas treatment and use, and the recovery of byproducts.

The ammonia recovered from coal gas was long the chief commercial source of ammonia and its compounds. This situation changed quite decidedly upon the development of improved processes for the synthesis of ammonia from nitrogen and hydrogen, but byproduct ammonia from coal carbonization plants still remains an important commercial commodity.

It should be emphasized that ammonia is removed from coal gas not only as a recovery of a useful byproduct but also because the presence of large amounts of ammonia in gas distributed for city use has a deleterious effect on parts of the distri-

37 Ellis, C., *The Chemistry of Synthetic Resins,* Vol. I, Reinhold Publishing Corp., New York, 1935, 829 pp.

bution system and appliances, especially brass parts of meters and other fixtures with which the gas comes in contact and also leather meter diaphragms.[10] For this reason many states require that the ammonia content of gas for city use shall not exceed 0.016 or 0.031 percent by volume, which means that 97 percent or more of the ammonia originally present in the crude coal gas must be removed simply to conform to state regulations, and entirely aside from the recovery of a byproduct.

In the usual high-temperature carbonization of coal, approximately 15 to 20 percent of the nitrogen of the coal appears in the crude coal gas as ammonia. An average figure would be 5.5 pounds of ammonia per ton of coal or about 0.5 pound per 1,000 cubic feet of coal gas. This corresponds to 1.1 percent by volume of the crude coal gas. The various factors affecting the ammonia yield, such as type of coal, temperature of carbonization, and steaming of the charge, have been discussed in other chapters.

Because ammonia is very soluble in water it begins to leave the gas as soon as the crude coal gas comes into contact with water or condensation of water from the gas occurs. Not only does it occur in this water as free ammonia, but also rather loosely combined with weak acids, as carbon dioxide, hydrogen sulfide, and hydrocyanic acid, and also as "fixed ammonia," that is, ammonium chloride, etc. This ammoniacal water, known as "weak ammonia liquor," is discussed in some detail in Chapter 27. Rather comprehensive treatments of the subject are also given in all books on gas manufacture.[2, 4, 6, 8]

Hydrocyanic acid occurs in all high-temperature-carbonization coal gas, being chiefly a secondary product resulting from the reaction between ammonia in the gas and the hot carbon in the retort or oven.

In the gas industry, this compound is often rather loosely referred to as "cyanogen."

The amount of hydrocyanic acid present in the crude coal gas varies from 0.10 to 0.25 percent by volume. Like ammonia, although quantitatively to a lesser extent, hydrocyanic acid is soluble in water, so that the content of this compound in the gas continuously decreases through the gas-treatment system as the gas comes into contact with water or as water condenses from the gas. Although the compound dissolves in the ammonia liquor condensate as a cyanide, it very readily changes into a thiocyanate as a reaction product with sulfur compounds, and it is mostly found in this form.

Aside from the incidental removal of hydrocyanic acid in the condensate and scrubbing water with which the gas may come in contact during treatment in the plant, the removal of this compound is not universally practiced by any means. However, a very considerable decrease in the hydrocyanic acid content of the gas usually occurs coincident with the removal of hydrogen sulfide. With the iron oxide system of purification the decrease in hydrocyanic acid content may be only a minor proportion, but with liquid purification processes, the removal may be 90 percent or more. This is discussed in detail in Chapter 26 on the removal of sulfur compounds from coal gas. In Chapter 27, describing the removal of nitrogen compounds from coal gas, the commercial processes for the recovery of cyanogen compounds as useful byproducts are discussed.

From the above it may be seen that the hydrocyanic acid content of the treated coal gas, ready for distribution to a city, may vary from an extremely small amount to an amount but little lower than that in the crude coal gas. The chief deleterious effect of this compound in the distributed

gas is its tendency to contribute to certain types of corrosion in the gas mains and customer appliances. Although the hydrocyanic acid does not appear to initiate corrosion, it contributes to the effect in combination with oxygen, sulfur compounds, etc.[38]

Other than hydrocyanic acid, extremely small amounts of other cyanogen compounds are presumed to be present in coal gas. Among these might be mentioned cyanogen, C_2N_2, and acetonitrile, CH_3CN. No conclusive study has been made of these compounds in coal gas, this being a good subject for future investigation.

The most important organic nitrogen constituents of coal gas are pyridine and its various homologs, such as the picolines and lutidines. Although not found in large quantities in coal gas, nevertheless this has been an important source of these compounds, and very recently new uses for these organic bases have revived interest in their recovery.

A typical figure for the content of total pyridine bases in raw coal gas is 0.014 pound per 1,000 cubic feet of gas.[39] However, about 40 percent of this material condenses out with the tar, so that the pyridine content of the gas just before the ammonia scrubbers or saturators would be about 0.008 pound per 1,000 cubic feet. This is equivalent to about 0.004 percent by volume. In the recovery of ammonia from the gas some of the pyridine is absorbed and constitutes an impurity of the aqua ammonia or the ammonium sulfate. Of the total pyridine bases in the gas usually 70 percent or less is pyridine, the remainder being a mixture of various other bases, such as the picolines, which have higher boiling points than pyridine.

Methods for recovery of the pyridine bases from coal gas are described in Chapter 27.

Sulfur Compounds. Since coal always contains sulfur, coal gas as it leaves the carbonizing chamber is never free of sulfur compounds. Furthermore, the amount of sulfur compounds in the gas is roughly proportional to the sulfur contained in the coal. Detailed references to the forms of sulfur in coal and the reactions leading to sulfur compounds in the gas are given in Chapter 26.

Nearly all, usually well over 95 percent, of the sulfur in the raw coal gas is in the form of hydrogen sulfide. Most of the remainder is present as carbon disulfide. Other sulfur compounds are found in coal gas in only minute quantities, and probably even these are not always present.

Depending largely on the sulfur content of the coal being carbonized, the hydrogen sulfide in raw coal gas will vary from 0.3 to 3.0 percent by volume, but 0.6 percent by volume is typical and representative of most commercial coal gas. Although hydrogen sulfide is a gas and not a condensable vapor, it is soluble to some extent in the condensed ammonia liquor. However, on distillation of the ammonia liquor the hydrogen sulfide is evolved and thence often returns to the gas stream. Usually, therefore, except in the indirect system of ammonia recovery, hydrogen sulfide is not removed in the condensation system of the plant.

Where gas is distributed for city use, practically all the hydrogen sulfide must be removed before the gas leaves the plant. Regulations in most states call for a maximum of about 0.0005 percent by volume or less in the purified gas. Even coal gas that is not distributed for city use is sometimes

[38] Murphy, E. J., *Gas Age*, **84**, No. 11, 23-7 (1939); *Am. Gas J.*, **151**, No. 6, 9-13, 41 (1940).
[39] Klempt, W., and Röber, R., *Chem. Fabrik*, **13**, 65-84 (1940).

purified of hydrogen sulfide, at least to some extent.

This necessity for removal has encouraged the development of many processes for purifying gas of its hydrogen sulfide content. Some of these processes simply remove the impurity from the gas with no attempt at recovery, but the newer ones not only remove the hydrogen sulfide but also secure the recovery of the sulfur in some economically useful form. This subject is so important that it is discussed in considerable detail in Chapter 26.

Carbon disulfide occurs in raw coal gas in amounts ranging from 0.007 to 0.07 percent by volume, the quantity being largely dependent on the sulfur content of the coal and the conditions of carbonization. A typical figure for carbon disulfide in raw coal gas is 0.015 percent by volume. When coal is carbonized in coke ovens, the total organic sulfur present in the raw coal gas accounts for 1.0 to 1.8 percent of the sulfur present in the coal charged to the ovens.[40]

The origin of the carbon disulfide in coal gas has been extensively investigated by Huff and Holtz.[41] Their explanation is that hydrogen sulfide passing over the hot carbon in the carbonizing chamber first forms a carbon-sulfur complex on the surface of the carbon, and, after this complex has reached a sufficient concentration, the sulfur is volatilized into the stream of coal gas in the form of carbon disulfide.

Since carbon disulfide is a vapor, a portion is removed from the coal gas in connection with the removal of light oil. The percentage so removed varies with the conditions in the light-oil scrubbers, but usu-

ally a very considerable proportion is taken from the gas at this point. Therefore, where light-oil removal is practiced, the carbon disulfide content of the coal gas leaving the plant will be very substantially less than the figures mentioned previously for raw coal gas.

Special processes for the specific removal of organic sulfur and more particularly carbon disulfide have been installed in a few coal-gas plants, although the operation today is a rather rare exception in America. In England removal of organic sulfur is much more common. A description of these processes is also given in Chapter 26 of this book.

The chief objection to the presence of carbon disulfide and other organic sulfur compounds in gas is the fact that sulfur dioxide is produced on combustion of the gas, which may cause corrosion of metals, etc. State regulations often restrict the content of organic sulfur in gas distributed for city use to 0.025 percent by volume, calculated as volume of carbon disulfide.

Other than carbon disulfide, organic sulfur compounds in coal gas are of little importance. As a matter of fact, only one or two thorough investigations have been made of these minor sulfur compounds. In England a rather comprehensive study was made in connection with the development of processes to remove organic sulfur from coal gas.[42] In mixed coal gas from vertical and inclined retorts, the following amounts of organic sulfur compounds were found, expressed as grains of sulfur per 100 cubic feet of gas: mercaptan, 1.8; thiophene, 6.1; carbon disulfide, 18.7; volatile sulfur compounds, 5.4; total, 32.0.

Assuming that the "volatile sulfur compounds" represent carbon oxysulfide, the following figures give the percent by vol-

40 Brysch, O. P., and Byrne, J. F., *Proc. Am. Gas Assoc.*, **1927**, 1463-71.

41 Huff, W. J., *Ind. Eng. Chem.*, **18**, 357-61 (1926). Holtz, J. C., *Origin and Decomposition of Organic Sulfur Compounds under Gas Making Conditions*, Johns Hopkins Univ. Press, Baltimore, Md., 1930, 83 pp.

42 Hollings, H., Hutchison, W. K., and Griffith, R. H., *Gas J.*, **220**, 475-85 (1937).

ume of each compound in this particular gas: mercaptans, 0.003; thiophene, 0.010; carbon disulfide, 0.016; carbon oxysulfide, 0.009.

Mercaptans in gas denote a lower range of carbonization temperatures, and usually they are not present in detectable quantities in coke-oven gas produced at higher temperatures.

Thiophene, because of its relatively low vapor pressure (about the same as benzene), is largely removed with the light oil and on distillation remains in the benzene fraction. Because of this fact, it is often an undesirable impurity in light oil, and methods have been developed for its removal from light oil. (See Chapter 28.)

Carbon oxysulfide, COS, is probably present in all high-temperature coal gas to some extent, at least. Very little information is available regarding this compound in coal gas, so that an almost virgin field of research is open on the subject.

Various sulfides and disulfides are also presumably in coal gas, but again the subject has been but superficially investigated. As a matter of fact, the entire subject of the minor organic sulfur compounds of coal gas should be thoroughly gone into, since this information is of more than ordinary importance in connection with the development of processes to remove organic sulfur from gas.

REMOVAL OF SULFUR COMPOUNDS FROM COAL GAS

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All commercial coal gases contain sulfur compounds, since all commercial coals used for coal-gas manufacture contain significant quantities of sulfur. The following sulfur compounds have been identified in coal gas:[1,2,3] (1) hydrogen sulfide, H_2S; (2) carbon disulfide, CS_2; (3) thiophene, C_4H_4S, and its homologs, mainly methyl thiophenes, $CH_3 \cdot C_4H_3S$; (4) carbon oxysulfide, or carbonyl sulfide, COS; (5) mercaptans or thiols, mainly ethyl mercaptan, $C_2H_5 \cdot HS$, and methyl mercaptan, $CH_3 \cdot HS$; (6) thio ethers, such as dimethyl sulfide, $CH_3 \cdot S \cdot CH_3$; and (7) disulfides, such as methyl disulfide, $CH_3 \cdot S \cdot S \cdot CH_3$.

Hydrogen sulfide is the principal sulfur compound present in coal gas. Usually around 90 to 95 percent of the total sulfur in coal gas is in this form.

The gas industry uses the term "organic sulfur" to designate all sulfur compounds other than hydrogen sulfide that are present in coal gas. "Organic sulfur" has been used synonymously with carbon disulfide,

although it is not strictly correct to do so. About two-thirds of the "organic sulfur" is in the form of carbon disulfide. Thiophenes occur in only small concentrations and are of importance mainly because they accompany and contaminate the benzol and the toluol recovered from coal gas. For more information on these compounds, reference should be made to Chapter 28. The other sulfur compounds also occur in very small concentrations. Usually, the "organic sulfur" compounds are of importance only when a gas of very low sulfur content is desired or when coals of high sulfur contents are used.

The presence of hydrogen sulfide and other sulfur compounds in gas is objectionable for various reasons. Hydrogen sulfide causes drip-water to be corrosive, and it is also corrosive to metal devices in smaller gas meters and other equipment for handling gas. The products of combustion of gas in which there are sulfur compounds contain sulfur dioxide and sulfur trioxide, compounds that have a disagreeable odor and are corrosive.

The early processes for removing sulfur compounds from gas were entirely for the purpose of eliminating the odor in the products of combustion. Little thought was given to the recovery of the sulfur itself. The sulfur-containing waste material was

[1] Hutchinson, W. K., *Gas J.*, **220**, 476–80 (1937). Hollings, H., Hutchinson, W. K., and Griffith, R. H., *Inst. Gas Engrs., Commun.* **175** (1937), 64 pp.

[2] Huff, W. J., *Proc. 2nd Intern. Conf. Bituminous Coal*, **2**, 814–25 (1928). Bakes, W. E., King, J. G., and Sinnatt, F. S., *Dept. Sci. Ind. Research (Brit.), Fuel Research Tech. Paper* **31** (1931), 35 pp.

[3] King, H. S., and Maddock, F. B., *Can. Chem. Process Ind.*, **23**, 3–4 (1939).

later found to have value depending upon its sulfur content. Where the price level of sulfur was sufficiently high, or where waste disposal was sufficiently expensive, recovery of the sulfur in some form has been practiced.

In recent years, more extensive work has been done on different methods for both removing and utilizing the hydrogen sulfide and other sulfur compounds. Sulfur compounds have been utilized principally by conversion to elemental sulfur of value for fungicidal and chemical purposes, by the recovery of pure hydrogen sulfide for chemical uses, and by the conversion of the sulfur together with the ammonia also present in coal gas to ammonium sulfate or similar compounds of commercial value. Details of these developments are discussed later.

SOURCES AND AMOUNTS OF SULFUR COMPOUNDS IN COAL GAS

The sulfur present in coal gas, of course, comes from the sulfur compounds in the coal that is carbonized. The amount and distribution of the various gaseous sulfur compounds formed during carbonization depend on several factors, such as: (1) types and amounts of sulfur compounds in the original coal; (2) characteristics of the ash content of the coal; and (3) conditions during carbonization, such as moisture content, temperature, amount and time of contact between the gases and the hot coke, the length of time the gases remain inside the coking chamber, and the types of other compounds present in the coal gas. Various investigations have been made in an attempt to correlate the types of sulfur in the coal with the amounts and types of sulfur in the gas, but, because of the number of factors involved, the work merely confirms the complexity of the subject.

Actual operating results in coke ovens

and gas retorts that have been reported [4,5] indicate that: (1) from 50 to 65 percent of the sulfur that is present in the coal is retained by the coke, though the percentage may be still higher; (2) from 25 to 30 percent of the sulfur forms hydrogen sulfide, H_2S, in the gas; and (3) from 1.0 to 1.5 percent of the sulfur forms carbon disulfide and other "organic sulfur" compounds. The higher percentage figure tends to result from higher sulfur contents and higher temperatures. The balance of the sulfur is present in the tar and in the ammonia liquor.

The following relationships will serve as a rough guide for predicting the approximate sulfur contents of coal gas: (1) the hydrogen sulfide content of gas, in grains per 100 cubic feet, equals 365 times the percentage of sulfur in the coal; and (2) the organic sulfur content of gas, in grains of sulfur per 100 cubic feet, equals 18 times the percentage of sulfur in the coal. In using these relationships, it must be kept in mind that they are only approximate and are roughly correct for coals ordinarily used in coke ovens and gas retorts in America and for ordinary operating conditions. Changes in coking conditions and coals other than coking coals of the Appalachian region may produce results differing from the above.

A sulfur balance made at a coke plant carbonizing coal of 0.79 percent sulfur is shown in Table I. In Table II are shown the relationships between the "organic sulfur" in the coal gas and the sulfur content of the coal. These data were reported by Brysch and Byrne [5] and by Sperr.[5]

4 Meade, A., *Modern Gasworks Practice*, Benn Bros., London, 1921, 815 pp.

5 Brysch, O. P., and Byrne, J. F., *Proc. Am. Gas Assoc.*, **1927**, 1463–7. Dawson, K. L., *Eng. J.*, **1928**, 266. Sperr, F. W., Jr., *Proc. 2nd Intern. Conf. Bituminous Coal*, **2**, 37–64 (1928).

TABLE I

SULFUR BALANCE MADE ON KOPPERS OVENS
OF THE CHICAGO BYPRODUCT COKE COMPANY [5]

	Pounds of Sulfur	Percentage of Total Sulfur Entering Oven
Sulfur entering oven		
(22,500 pounds coal of 4.7 percent moisture and 0.79 percent sulfur)	169 0	100.0
Sulfur leaving oven		
In coke (15,350 pounds dry coke of 0.65 percent sulfur)	100 3	59 4
In gas		
Organic sulfur (16 grains per 100 cubic feet)	2 4	1 4
Hydrogen sulfide (325 grains per 100 cubic feet)	46 3	27 4
Ammonia liquor, tar, and unaccounted for (by difference)	20 0	11 8
Total	169 0	100 0

The amounts of the different sulfur compounds in the group of compounds called "organic sulfur" have not been investigated thoroughly. In tests reported by Hutton and Thomas,[6] coal was carbonized in a standard D-retort and about 80 percent of

[6] Hutton, U O, and Thomas, C C, *Gas Age*, 47, 88 (1921).

the organic sulfur content was found to be included in the group carbon disulfide, carbon oxysulfide, and mercaptans. No attempt was made to separate these compounds. Work reported by Hutchinson [1] showed the organic sulfur contents of gas made by carbonizing English coal in inclined and vertical retorts. The amounts and distribution of the different sulfur compounds are given in Table III.

The conditions existing in gas retorts are obviously different from those existing in coke ovens. Under the higher temperature conditions in gas retorts, it would be expected that there would be greater quantities of the sulfur compounds that are more stable at higher temperatures, and it is generally recognized that thiophene, carbon oxysulfide, and carbon disulfide are high-temperature products. Consequently, the proportions shown in Table I cannot be used directly for estimating the proportions of sulfur compounds in coke-oven gas.

Some work by Shaw [7] has shown the following sulfur content of debenzolized

[7] Shaw, J A, private communication

TABLE II

RELATION BETWEEN SULFUR CONTENT OF COAL AND ORGANIC SULFUR IN GAS MADE IN KOPPERS OVENS [5]

Test	Percentage of Sulfur in Coal	Percentage of Volatile in Coal	Organic Sulfur in Gas		
			Grains Sulfur per 100 Cubic Feet	Percentage of Total Sulfur in Coal	Grains per 100 Cubic Feet per Percent Sulfur in Coal
A	4.56	· 33.0	103	1.8	22.6
B	3.59	31.7	67	1.4	18.6
C	3.65	29.9	51	1.0	14.0
D	1.80	24.6	28	1.0	15.6
E	1.74	27.4	30	1.2	17.2
F	0.79	29.1	16	1.4	20.2
G	0.93	28.8	19	1.4	20.4
Average				1.3	18.4

TABLE III

ORGANIC SULFUR COMPOUNDS IN COAL GAS FROM RETORTS AND OTHER GASES [1]

Type of Retort or Gas Manufacturing Equipment	Total Organic Sulfur, grains per 100 cubic feet	Distribution of Organic Sulfur among Different Compounds (in percent of total organic sulfur)			
		Mercaptans	Thiophene	CS_2	Volatile Sulfur Compounds *
Vertical retorts, continuous	31.7	4.4	12.0	66.3	17.3
	23.6	4.2	15.7	61.5	18.6
	29.4	5.4	17.4	59.0	18.3
Vertical retorts, intermittent	20.1	6.0	16.4	53.6	24.0
Inclined retorts	31.2	3.5	26.6	54.2	15.7
Horizontal retorts	34.5	4.1	18.3	67.2	10.4
Horizontal retorts, steamed	35.6	6.5	22.0	56.3	15.2
Coke ovens	25.2	...	....	....	13.5
Carburetted water gas	11.7	3.4	30.8	17.1	48.7

* "Volatile sulfur compounds" were described by the authors as compounds not removable by oil washing. Since carbon oxysulfide is the only sulfur compound (other than hydrogen sulfide) that has been identified in coal gas and that is not removable by oil washing, it can be assumed that this is actually carbon oxysulfide.

coke-oven gas made from a coal mixture containing 0.7 percent sulfur:

	GRAINS SULFUR PER 100 CUBIC FEET
Carbon disulfide	3.8
Carbon oxysulfide	0.9
"Other organic sulfur"	0.6
Total "organic sulfur"	5.3

In this tabulation, the term "other organic sulfur" includes thiophene, mercaptans, disulfides, and thio ethers of which thiophene is the predominating compound. The light oil which had been scrubbed out of the gas analyzed in these tests ordinarily contained, per 100 cubic feet of gas scrubbed:

	GRAINS SULFUR PER 100 CUBIC FEET OF GAS
Thiophene	0.8
Carbon disulfide	3.5

Accordingly, the gas before the light oil recovery equipment contained:

	GRAINS SULFUR PER 100 CUBIC FEET
Carbon disulfide	7.3
Carbon oxysulfide	0.9
Thiophene and other organic sulfur compounds	1.4
Total organic sulfur	9.6

FORMATION OF SULFUR COMPOUNDS DURING COAL CARBONIZATION

The original sulfur in coal is considered to exist in three different forms: (1) pyritic sulfur, or sulfur combined as pyrite and marcasite; (2) organic sulfur, or sulfur combined with the coal substance; and (3) sulfate sulfur, or sulfur combined as calcium and iron sulfates.

When the coal is carbonized, these sulfur compounds in the coal are decomposed by the temperature and by reaction with the products of coal decomposition. The primary gaseous compounds of coal distillation are further altered by temperature and contact with incandescent coke and oven walls and by contact with other gases from

the coal. Consequently, conditions within the oven or retort are rather complex, and the variety and amounts of the sulfur compounds finally leaving the coke oven or retort are the overall result of several reactions and equilibriums. The nature of the mineral matter in the coal may be a major factor affecting the amount and types of gaseous sulfur compounds formed,[8] as appears reasonable in the light of experimental work on the synthesis of various organic sulfur compounds.

Various workers [9] have shown that equilibrium conditions exist for reactions between hydrogen sulfide and various hydrocarbons such as methane, ethane, acetylene, and ethylene. Since sulfur compounds in gas, other than hydrogen sulfide and carbon disulfide, occur only in very small concentrations, it seems very plausible that their final concentrations in the coal gas depend upon equilibriums of hydrogen sulfide with various hydrocarbons and upon the presence in the coal of catalytically active material that helps the gases to approach these equilibriums. The presence of these various sulfur compounds in coal gas consequently does not necessarily indicate that they are formed from definite types of sulfur compounds in the original coal. The concentrations and types of sulfur compounds in the coal gas leaving the ovens depend on several conditions, including (a) the types and amounts of sulfur compounds originally formed when the coal is heated; (b) the temperature to which the gases are heated before leaving the oven; (c) the types of hydrocarbons present in the gases; (d) the

amount of contact between the gases and incandescent coke; and possibly (e) the type of mineral matter in the coke.

Studies have been made to determine whether the evolution of sulfur in the gaseous products is influenced by the chemical form in which the sulfur exists in the coal.[10] Some differences were noted in the amounts of different gaseous sulfur compounds formed from different types of coal-sulfur under conditions prevailing in the laboratory carbonization experiments. In actual coke-oven conditions, the secondary reactions mentioned in the preceding two paragraphs appear to have the predominating influence in determining the total quantities and relative amounts of the gaseous sulfur compounds. Practically, Powell [10] concluded that the form in which sulfur exists in coal has little effect on its evolution during coking in actual byproduct ovens.

IDENTIFICATION AND ANALYSIS OF SULFUR COMPOUNDS

Hydrogen Sulfide. Methods of analysis of gas to determine the amounts of hydrogen sulfide are given in reference books on the subject.[11] The methods usually depend on one of the following: (1) Hydrogen sulfide is quantitatively precipitated as cadmium sulfide by neutral or alkaline solutions of a cadmium salt, and the amount of sulfide is then determined by oxidation with acidified iodine. (2) Hydrogen sulfide is absorbed by caustic solutions, forming soluble sulfides, and the amount of sulfide is determined by oxidation with acidified iodine. (3) Hydrogen sulfide is quantitatively oxi-

8 Himus, G. W., and Egerton, A. C., *Iron & Coal Trades Rev.*, 138, 663-4 (1939). Himus, G. W., and Armstrong, V., *Chemistry & Industry*, 17, 543 8 (1939).

9 Roelen, O., *Brennstoff-Chem.*, 12, 305-12 (1931). Schneider, G. G., Bock, H., and Hausser, H., *Ber.*, 70B, 425-9 (1937). Jones, S. O., and Reid, E. E., *J. Am. Chem. Soc.*, 60, 2452-5 (1938).

10 Powell, A. R., *J. Ind. Eng. Chem.*, 12, 1069-76 (1920). Snow, R. D., *Ind. Eng. Chem.*, 24, 903 9 (1932). Woolhouse, T. G., *Fuel*, 14, 259-95 (1935).

11 American Gas Association, *Gas Chemists' Handbook*, American Gas Association, New York, 3rd ed., 1929, 795 pp.

dized by iodine to sulfur and hydriodic acid, in neutral or acid solution. (4) A lead acetate paper exposed to gases containing hydrogen sulfide darkens owing to the formation of black lead sulfide. The darkness of the stain depends upon the amount of hydrogen sulfide present. This method is usually used for the estimation of very small amounts of hydrogen sulfide, or to demonstrate that the gas contains but a minute amount of hydrogen sulfide.

The general methods 1 and 2 have been studied by Shaw and have been found to give somewhat irregular results. This is due to two causes: mercaptans in the gas are partially or wholly included with the hydrogen sulfide, depending on conditions such as acidity of the cadmium solution; and the reaction between hydrogen sulfide and iodine is quantitative only in acid solution. Shaw [12] described an apparatus and technique that improve the accuracy of this method and also make possible the determination of sulfides in any alkaline solution with greater accuracy than with previous methods. In this technique, the solution is acidified and mixed before any iodine is added, thus eliminating all possibility of reactions between alkaline solutions and iodine—probably the greatest source of error when acidified iodine is used in the conventional methods.

Lead acetate paper methods have been studied by various investigators.[13] [19] Methods of this type, as previously stated, may be used either to detect the presence of small amounts of hydrogen sulfide in gas or to measure small amounts of hydrogen sulfide.

A lead acetate paper method is almost generally employed in the United States to determine whether gas is sufficiently free from hydrogen sulfide to satisfy legal requirements for domestic use; it is an empirical method, and an exact procedure for making the test has been specified.[11, 20] The procedure must be followed exactly to obtain consistent results, especially when the hydrogen sulfide content approximates the amount that can just be detected by that method. Gas that passes this test contains less than about 0.5 grain hydrogen sulfide per 100 cubic feet.[20]

More recent study of lead acetate paper methods has been made mainly with three objectives in view: first, to study the conditions affecting the sensitivity of the tests; second, to improve the accuracy of methods using lead acetate to determine quantitatively small concentrations of hydrogen sulfide; and, third, to develop recording instruments to show the presence or absence of detectable concentrations of hydrogen sulfide. Truesdale [17] and Leroux [18] have studied factors that affect the sensitivity of lead acetate paper tests. The presence of hydrogen sulfide is easier to detect in hydrogen gas than in nitrogen, and, in turn, in nitrogen than in carbon dioxide. Leroux reported that the lowest concentrations detected by the lead acetate method in his apparatus were:

12 Shaw, J. A., *Ind. Eng. Chem., Anal. Ed.,* **12,** 668–71 (1940).

13 Gas Light and Coke Co., So. Metropolitan Gas Co., *Gas World,* **103,** 386–8 (1935).

14 Anon., *Het Gas,* **48,** 281 (1928)   Kraus, R., *Chem. Fabrik,* **9,** 241–2 (1936). Reed, J. B., *J. Soc. Chem. Ind.,* **57,** 43–4 (1938). Norgate, R., Brit. Pat. 426,378 (1938).

15 Littlefield, J. G., Yant, W. P., and Berger, L. B., *U. S. Bur. Mines, Repts. Investigations* **3276** (1935), 13 pp.

16 Hollings, H., and Hutchinson, W. K., *Gas World,* **102,** 676–81 (1935).

17 Truesdale, E. C., *Ind. Eng. Chem., Anal. Ed.,* **2,** 299–302 (1930).

18 Leroux, H., *J. usines gaz,* **55,** 117–22 (1931).

19 Bach, H., *Gas- u. Wasserfach,* **72,** 154–5 (1929).

20 McBride, R. S., and Edwards, J. D., *Natl. Bur. Standards U. S., Tech. Paper* **41** (1914), 46 pp.

	GRAINS PER 100 CUBIC FEET
H₂S in hydrogen	0.05
H₂S in nitrogen	0.3
H₂S in carbon dioxide	1.6

Direct impingement of a capillary jet of gas on or through a lead acetate paper is a much more sensitive method than exposure of the paper to the gas in a less thorough manner. The use of dry gas and wet paper or of dry paper and wet gas, and of alkaline lead acetate, makes the test more sensitive. The lowest concentration of hydrogen sulfide to cause a definite test in an extremely sensitive method followed in Truesdale's experiments was 0.00002 percent hydrogen sulfide or 0.012 grain per 100 cubic feet. Gas containing 0.006 grain per 100 cubic feet caused stains that were possibly faintly perceptible, and gas containing 0.002 grain per 100 cubic feet definitely would not produce a stain regardless of how much gas was impinged on the paper.

Hollings and Hutchinson [16] described an apparatus for making a lead acetate paper test and a technique of measuring the optical density of the lead acetate paper stain to determine small concentrations of hydrogen sulfide in coal gas. The term "optical density" was used to indicate the degree of absorption of light transmitted through the paper containing the stain and should not be confused with the appearance of the stain by reflected light. Different forms of apparatus [14] have been devised for making lead acetate paper tests continuously or at regular intervals and recording the presence or absence of a stain photoelectrically.

Lead acetate on materials other than paper, and other reagents than lead acetate, have been studied. The U. S. Bureau of Mines [15] has developed a detector for hydrogen sulfide using activated alumina coated with lead acetate, which is useful through the range of hydrogen sulfide concentrations of 1.5 to 30 grains of H₂S per 100 cubic feet. Reagents such as silver salts, sodium nitroprusside, and para-aminodimethylaniline have been studied, and they may be useful under certain conditions. In general, lead acetate has the advantage of high sensitivity combined with permanence of the stain in the presence of oxygen.

High concentrations of hydrogen sulfide can be measured by iodimetric and by absorption methods. The Tutweiler method described in the *Gas Chemists' Handbook* [11] can be modified by using a 0.08 N iodine solution; this modification has proved satisfactory for the analysis of concentrated hydrogen sulfide recovered from coke-oven gas.

Organic Sulfur. As mentioned previously, the expression "organic sulfur" as employed by the gas industry includes all sulfur compounds in fuel gas other than hydrogen sulfide. Consequently, organic sulfur is determined by finding the total sulfur after removing the sulfur present as hydrogen sulfide. The ordinary method for this purpose is the so-called referee's method originally developed about one hundred years ago and described in the *Gas Chemists' Handbook*.[11] In this, and in modifications such as the Drehschmidt method, a measured amount of gas is burnt and the sulfur dioxide in the products of combustion is measured.

The technique originally developed by Harcourt [21] for the determination of carbon disulfide has been further developed for the rapid determination of all sulfur compounds in gas. In this method, the hydrogen sulfide is first removed, and the remaining sulfur compounds are converted catalytically to hydrogen sulfide. The amount of hydro-

21 Abady, J., *Gas Analyst's Manual*, E. & F. N. Spon, London, 1902, 561 pp.

gen sulfide thus formed is then measured. A newer technique for this method has been described by Lusby,[22] who catalyzed the conversion to hydrogen sulfide by means of a heated platinum spiral. This method must be applied only to a gas high in hydrogen. Modified techniques for this method substitute platinized asbestos [23] or activated alumina [24] for the platinum spiral. Also, it has been recommended [25] that the gases be highly humidified before passing the platinum spiral to obtain more nearly complete conversion to hydrogen sulfide. Saturating with water at 80 to 90° C is proposed. Russell [26] reported that the platinum spiral method is suitable when the hydrogen content is over 25 percent and the illuminants are under 8 percent.

Since examination of coal gas has shown that the so-called organic sulfur actually includes several sulfur compounds, investigators have developed methods for identifying the different compounds. Desy [27] has described a rapid method for determining the carbon disulfide in gas colorimetrically by converting the carbon disulfide to cupric xanthate and measuring the color. The Chemical Department of the South Metropolitan Gas Company of London [28] has also published a method for the determination of carbon disulfide; in this method, a coloration is produced by reaction of the carbon disulfide with piperidine and a copper salt, and the color is compared with stand-ards. Results may be too high, however, in the presence of carbon oxysulfide, which produces a fading coloration. Avdeeva [29] described a method for determining both carbon disulfide and carbon oxysulfide in the presence of each other. King and Maddock [3] described the methods they employed to identify carbon disulfide, mercaptans, and thiophenes in coal gas. Hollings, Hutchinson, and Griffith [1] have also published the methods used or developed by them for measuring the mercaptan, thiophene, and carbon disulfide contents of coal gas.

OBJECTIONABLE FEATURES OF SULFUR COMPOUNDS IN GAS

The presence of sulfur compounds in gas has been considered objectionable from practically the beginning of the coal-gas industry. They are objectionable both in the gas before it is burnt and in the flue gases after combustion. Of the sulfur compounds, hydrogen sulfide is usually considered the only one causing objectionable conditions in the gas before combustion. It causes internal corrosion in gas mains, deteriorization of valves and tubing, especially brass and copper, and mechanisms exposed to gas atmospheres as in meters and regulators and special appliances. The blackening of metal surfaces, especially silver, when exposed to minute traces of hydrogen sulfide is well known. The products of combustion of all sulfur compounds, of course, contain sulfur dioxide and sulfur trioxide, and these gases are corrosive and obnoxious in odor.

Most municipal regulating bodies have definite requirements controlling the permissible concentration of sulfur compounds in domestic fuel gas. It is typical to require that the hydrogen sulfide content be low enough so as not to produce a stain on

22 Lusby, O. W., *Proc. Am. Gas Assoc.*, **1936**, 752–4.

23 Visser, G. H., and Engel, W. F., *II* *Congr. mondial petrole 2, Sect. 2, Phys. Chim. raffinage*, **1937**, 543–6.

24 Jilk, L. T., *Proc. Am. Soc. Testing Materials*, **39**, 1159–68 (1939).

25 Grimme, W., and Kock, E., *Chem.-Ztg.*, **63**, 870–1 (1938).

26 Russell, W. E., *Proc. Am. Gas Assoc.*, **1938**, 620–5.

27 Desy, G. G., *ibid.*, **1927**, 1440–1.

28 Chem. Dept., So. Metropolitan Gas Co., *J. Soc. Chem. Ind.*, **56**, 287–9 (1937).

29 Avdeeva, A. V., *Zavodskaya Lab.*, **7**, 279–81 (1938).

lead acetate paper when tested in a specified manner, that is, less than about 0.5 grain per 100 cubic feet. Requirements are not so severe, however, for organic sulfur; usually 15 to 30 grains total sulfur per 100 cubic feet are permitted.[30] States and municipalities have different requirements in this regard. The effect of organic sulfur requirements has been chiefly to prevent use of coals with excessive sulfur contents for domestic-gas manufacture.

The amount of corrosion by the products of combustion of coal gas depends on the flue system of the gas-burning appliance. When the products of combustion are cooled below their dew point, surfaces become wet with a sulfur-bearing water and corrosion is more severe. Parrish and Wood[31] have reported a series of tests in which coal gas containing about 25 grains total sulfur per 100 cubic feet was burned in different appliances; the amount of sulfur acids in the condensates was measured, and corrosion products were analyzed. The condensates in different types of calorimeters contained from about 15 to 75 percent of the sulfur present in the gas.

The deleterious effects of small amounts of sulfur in flue gases from gases of low sulfur content have been studied; an excellent résumé of the work of different investigators is given in the committee reports of the American Gas Association.[32, 33] The presence of but small amounts of sulfur in gas causes corrosion in the flue passages of gas appliances, such as water heaters and refrigerators. Occasional repairs and adjustments are consequently necessary to maintain the appliances in proper condition, the cost of which is usually borne by the gas companies. Kruger[32] concluded that the "sulfur must be reduced considerably below 2 grains per 100 cubic feet of fuel gas to eliminate corrosion problems."

Sulfur in coal gas utilized for certain other purposes is also objectionable. The amount of sulfur that can be tolerated differs for different applications. For example, gases used for melting glass need to be low in sulfur when glass of certain quality is being handled.[34] In gas-heated ovens for annealing glass, the formation of deposits of "bloom" on glassware had been blamed on small amounts of sulfur in the gas. Later work indicated that this "bloom" was due to other causes.[35] In certain heat-treatment processes of steel and other metals and alloys, even 7 to 10 grains per 100 cubic feet of organic sulfur cause difficulties.[36] For heating open-hearth furnaces and other furnaces for handling steels, excessive sulfur contents are undesirable. Ordinarily it had been considered permissible to use coal gas containing 550 to 700 grains sulfur per 100 cubic feet, although it was recognized that closer control of the furnaces was necessary with gases of higher sulfur content.[37] Gases of lower sulfur contents are more desirable, however, especially in making or handling steels of low sulfur specifications. Equilibriums between sulfur-bearing gases and melted steel have been studied by Maurer and Bischof.[38] In re-

[30] Anon., *Natl. Bur. Standards U. S., Circ.* **405** (1934), 258 pp.

[31] Wood, J. W., and Parrish, E., *Inst. Gas. Engrs., Commun.* **100** (1934), 47 pp.; *Gas J.*, **208**, 356–7, 527–30, 742–4 (1934).

[32] Kruger, R. E., *Proc. Am. Gas Assoc.*, **1930**, 517–42.

[33] Shnidman, L., *ibid.*, **1935**, 706–25. Shnidman, L., and Yeaw, J. S., *ibid.*, **1937**, 697–715, **1939**, 542–52. Murphy, E. J., *ibid.*, **1939**, 553–6.

[34] Kazanskii, M. S., *Keram. i Steklo*, **12**, 4–6 (1936).

[35] Memerey, E. J., *Proc. Am. Gas Assoc.*, **1931**, 1082–5. Shapley, C. S., *Gas World*, **105**, 538 (1936).

[36] Trutnovsky, H., *Gas- u. Wasserfach*, **78**, 462–5 (1935).

[37] Armstrong, H. C., *Trans. Second World Power Conf.*, Berlin, **2**, 288–96 (1930).

[38] Maurer, E., and Bischof, W., *J. Iron Steel Inst.*, **129**, 123–49 (1934).

viewing this subject in connection with the firing of open-hearth steel furnaces with coke-oven gas, Foxwell concluded that "clearly there are substantial advantages to be gained by bringing the sulfur content of the gases down to some 50 grains per 100 cubic feet, but from a metallurgical point of view there seems to be no particular point in removing the last few grains." [39]

The presence of sulfur compounds is undesirable also in the "bright annealing" of wire and similar products. When the total sulfur in the gas is too great an objectionable black sheen is formed on the surface of the metal. Such effects have been reported for gases containing no more than 15 grains of total sulfur per 100 cubic feet of gas. There are probably many industrial uses for coal gas in which gases of low sulfur contents are necessary.

HYDROGEN SULFIDE AND ITS REMOVAL

PROPERTIES OF HYDROGEN SULFIDE

Hydrogen sulfide at ordinary pressure and temperature is a colorless gas of characteristic odor reminiscent of rotten eggs. Physical properties of hydrogen sulfide, as given in different reference books,[40, 41, 42] are as follows:

Density:

1 liter at 0° C and 1 atmosphere weighs 1.539 grams.

1 cubic foot at 32° F and 1 atmosphere weighs 0.0961 pound.

1 cubic foot at 60° F and 30 inches weighs 638 grains or 0.09114 pound.

Specific gravity (air = 1.0), 1.190.

[39] Foxwell, G. E., *Gas World*, **104** (Coking Sect.), 69–75 (1936).

[40] *International Critical Tables*, McGraw-Hill Book Co., New York, 1928.

[41] *Annual Tables of Constants and Numerical Data*, Gauthier-Villars, Paris, 1934.

[42] Mellor, J. W., *Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Longmans, Green and Co., New York, 1930, Vol. X.

Density of liquid, 0.96 gram per cubic centimeter at −59.5° C.

Boiling point, −59.5° C or −75.1° F.
Freezing point, −82.9° C or −117.4° F.
Critical pressure, 88.9 atmospheres.
Critical temperature, 100.4° C or 212.7° F.

Vapor pressure:

°C	ATMOS-PHERES	MILLI-METERS	
−120	0.0092	7	
−100	0.0711	54	
−82.9	0.274	208	(melting point)
−80	0.325	247	
−60	0.973	740	
−59.5	1.00	760	(boiling point at 1 atmosphere)
−40	2.52		
−20	5.4		
0	10.2		
+20	17.2		
40	27.8		
60	42.2		
80	61.4		
100	88.3		
100.4	88.9	(critical point)	

Heat of combustion, at 60° F and 30 inches of mercury:

647 Btu per cubic foot or 7,100 Btu per pound, gross

596 Btu per cubic foot or 6,545 Btu per pound, net

Solubilities in water and organic solvents [43] at 20° C and hydrogen sulfide partial pressure of 1 atmosphere. (Solubilities are expressed as volumes of hydrogen sulfide reduced to 0° C and 1 atmosphere dissolved in 1 volume of saturated liquid.)

SOLVENT	SOLUBILITY
Water	2.554
Hexane	5.82
Cyclohexane	6.94
Benzene	14.5
Toluene	15.6
Alcohol	7.42

[43] Bell, R. P., *J. Chem. Soc.*, **1931**, 1371–82. Wright, R. H., and Maass, O., *Can. J. Research*, **6**, 94–101 (1932). Seidell, A., *Solubilities of*

TOXICITY OF HYDROGEN SULFIDE

Hydrogen sulfide is a poisonous gas. Its toxicity has been studied mainly in connection with the petroleum industry because many crude oils evolve gases with much higher concentrations of hydrogen sulfide than are encountered in coal gases. Authoritative general reviews of the subject of the toxicity of hydrogen sulfide are given in publications of the U. S. Bureau of Mines[44] and the U. S. Public Health Service.[45] In general, the effects of almost any toxic materials vary considerably with individuals and with other conditions, making it difficult to present exact figures. Because hydrogen sulfide paralyzes the sense of smell, it is dangerous to depend on its odor to determine whether toxic concentrations exist. The following figures give an approximate idea of permissible concentrations. The maximum permissible concentration of hydrogen sulfide for exposures not exceeding 8 hours per day is 1.3 grains per 100 cubic feet of air (20 parts per million by volume), according to the 1941 standard of the American Standards Association. Air containing around 3 grains of hydrogen sulfide per 100 cubic feet (0.0045 percent by volume) can be breathed for several hours before any toxic symptoms are produced. Breathing air containing 30 grains of hydrogen sulfide per 100 cubic feet (0.045 percent by volume) is dangerous and can possibly be fatal within 15 minutes. For a more explicit study of the physiological behavior of hydrogen sulfide, reference should be made to reports of various investigators.[46, 47] The treatment for hydrogen sulfide poisoning is also discussed by some of the above.[46] It is generally recognized that artificial respiration with oxygen inhalation is valuable first-aid treatment.

CORROSION DUE TO HYDROGEN SULFIDE

The corrosive nature of waters containing hydrogen sulfide is well known.[48] When gas containing hydrogen sulfide is cooled below its dew point, condensation of such waters occurs. Also, in handling concentrated hydrogen sulfide gas, as in processes for its recovery as such, condensation produces liquors containing hydrogen sulfide. Hydrogen sulfide is classified as an acidic gas, in that its solutions in water are weakly acidic. It forms insoluble black sulfides with many metals, including iron, copper, silver, and lead. When such a sulfide coating is formed, the coating may be, but is not necessarily, a protective coating. The sulfides, being electrical conductors, may also produce local couples and cause electrolytic corrosion.[49]

Usually, the corrosion due to hydrogen sulfide-containing waters is augmented by the presence of hydrocyanic acid and of oxygen. Many sulfides, iron sulfide especially, are oxidized by oxygen to form free sulfur and the oxide or hydroxide of the metal. This action both breaks down the protective coating and adds another ingre-

[46] Audibert, E., and Delmas, L., *Ann. mines,* (13), **2,** 203–13 (1933). Hunter, D., *Pharm. J.,* **137,** 514–5 (1936). Herbert, E. L., *J. Inst. Petroleum,* **25,** 323–46 (1939). McClurkin, T., *ibid.,* **25,** 382–91 (1939).

[47] Heering, *Gasmaske,* **8,** 88–9 (1936). DiBella, L., *Arch. fisiol.,* **37,** 291–318 (1937).

[48] Mills, R. van A., *U. S. Bur. Mines, Bull.* **233** (1925). 127 pp. Ott, E., and Hinden, F., *Monats-Bull. Schweiz. Ver. Gas- u. Wasserfach,* 1927, Nos. 1–2, 18 pp. Devine, J. M., Wilhelm, C. J., and Schmidt, L., *U. S. Bur. Mines, Tech. Paper* **560** (1933). 20 pp.

[49] Rhodes, F. H., and Johnson, E. B., *Ind. Eng. Chem.,* **16,** 575 (1924).

Inorganic and Metal Organic Compounds, D. Van Nostrand Co., New York, 1940, Vol. I.

[44] Katz, S. H., and Bloomfield, J. J., *U. S. Bur. Mines, Tech. Paper* **348** (1924), 37 pp. Sayers, R. R., *U. S. Bur. Mines, Bull.* **231** (1925), 108 pp.

[45] U. S. Pub. Health Service, *Pub. Health Repts.,* **56,** No. 14 (1941), 9 pp.

dient, sulfur, that contributes to corrosion. Various studies and observations indicate that, when the oxygen content is very low and when there are tar or oily films on the metal surfaces, conditions that ordinarily exist inside gas-handling equipment, corrosion is very slight.

As temperatures are increased to around 400° C or higher, dry hydrogen sulfide becomes corrosive to ordinary steel. Steels containing chromium are reported to be resistant to such corrosion. Below 400° C, only 3 percent of chromium is needed,[50] but at higher temperature it is necessary to have 12 to 20 percent chromium in the steel.[50, 51] Stainless steels containing 18 percent chromium and 8 percent nickel are also reported as satisfactory, but the presence of nickel does not add to their resistance to this type of corrosion.

RECOVERABLE SULFUR IN COAL GAS

According to the U. S. Bureau of Mines data, about 848,000,000 thousand cubic feet of coal gas were produced in byproduct coke ovens in the United States in the year 1940 from 77 million tons of coal. On the basis that each 1,000 cubic feet contains 0.5 pound of hydrogen sulfide (the average is probably somewhat higher), the total amount of hydrogen sulfide in these gases would be 424,000,000 pounds, or 212,000 tons, per year. This quantity of sulfur is about 7.5 percent of the annual production of mined sulfur in the United States and about one-third of the quantity of sulfur required for nonacid uses. Exact figures of actual sulfur recovery from coke-oven gas are not available, but rough estimates indicate that less than 10 percent of this available sulfur supply is being recovered and utilized.

Germany, in 1938, produced 48,500,000 tons of coke. According to the ratio 352 tons of coke per ton of sulfur in the coke-oven gas,[52] the sulfur-content of German coke-oven gas was 137,000 tons in that year. During the preceding year, 35,000 tons of sulfur were actually recovered, or about 30 percent of the sulfur content of the total German coke-oven gas.[53] Russia produced 23,200,000 tons of coke in 1938, or about one-half as much as Germany, and Great Britain produced 28,100,000 tons of coke including both gas retorts and byproduct oven coke, or about 60 percent of the German production. In Great Britain, from 70,000 to 80,000 tons of sulfur per year is extracted from fuel gases, the bulk of which is used for sulfuric acid manufacture.[54] Because of the anticipated military need for self-sufficiency in European countries, a larger part of the sulfur in European gas was being recovered than in the United States.

The bulk of the sulfur and hydrogen sulfide recovered from coke-oven gas in Europe is used for the production of sulfuric acid. In the United States, coke installations that operate processes for the recovery of elemental sulfur in a purer form market sulfur for agricultural sprays and for other fungicidal purposes,[55] as well as for use in the sulfite-pulp process in the paper industry. Some of the sulfur recovered by the ordinary iron oxide dry-box method is used for sulfuric acid manufacture, but most of such sulfur is discarded.

50 Ballabio, G., and Pastonesi, G., *Met. ital.*, **31**, 431–6 (1939).

51 White, A., and Marek, L. F., *Ind. Eng. Chem.*, **24**, 859–61 (1932).

52 Waeser, B., *Metalborse*, **23**, 333–4 (1933).

53 Reerink, W., *Gluckauf*, **74**, 303–9 (1938). Powell, A. R., *Ind. Eng. Chem.*, **31**, 789–96 (1939).

54 Avery, H. B., *Gas World*, **109**, 348–50 (1938).

55 Jacobson, D. L., *Chem. Markets*, **29**, 363–8 (1931). Sauchelli, V., *Ind. Eng. Chem.*, **25**, 363–7 (1933).

Very shortly after coal gas was introduced for a domestic fuel, it became apparent that its sulfur content was a decided disadvantage. Milk of lime was utilized for removing the sulfur compounds as early as 1809 in England by Clegg, two years after the first use of gas for street lighting. As can well be imagined, equipment using milk of lime would become plugged with solid deposits, and much trouble was encountered. Scrubbers using solid lime were employed a few years later.

Lime, of course, removes the acid-forming ingredients from the gas, namely, carbon dioxide, hydrogen sulfide, and hydrocyanic acid. After the lime has become saturated with these gases, further contact with the gas will not result in the absorption of more hydrogen sulfide. Instead, the spent lime will actually absorb more carbon dioxide and expel hydrogen sulfide that was previously absorbed. Hence it is necessary to exercise careful control to remove the spent lime promptly. The disposal of the spent lime is also troublesome for the same reason, as it absorbs carbon dioxide from the air and releases hydrogen sulfide.

During the period that lime purifiers were utilized it was also discovered that *sulfided* lime would absorb some carbon disulfide, a material that is not absorbed by the *unsulfided* lime. Because British coals ordinarily contained sufficient sulfur to produce a gas of objectionably high carbon disulfide content, the technique of using sulfided lime for carbon disulfide removal was developed. The British "Sulfur Act of 1860" was placed in force to insure careful operation of these sulfided lime scrubbers to remove carbon disulfide. This act set a maximum permissible sulfur content of but 17 to 22 grains per 100 cubic feet. Although this act did much to improve the quality of the gas actually distributed, it also prevented the British gas industry from completely replacing the lime purifiers by the more economical and less troublesome iron oxide purifiers. In 1905, the old gas Sulfur Act of 1860 was replaced with a new act, as a result of which the old lime purifiers have been entirely replaced by oxide purifiers except in some smaller installations.

Iron oxide was developed by Laming and Hills and patented in 1849. About fifteen years later, lime purifiers on continental Europe were being replaced by iron oxide boxes. Around the year 1870, iron oxide purifiers began to be adopted in the United States. The first iron oxides were chemically prepared. Later, bog iron ores were also used, and still later byproduct iron oxides from other industries came on the market. Methods for the chemical preparation of oxides have been improved to yield better products, and byproduct oxides have also been improved; as a result, all types of iron oxide remain in use.

The design and operation of dry iron oxide purifiers have not changed fundamentally since the early installations. However, as the result of investigations more intelligent control can be exercised, and the type of oxide has been improved to increase capacity.

Liquid purification processes, that is, processes in which hydrogen sulfide is washed from the gas by means of liquids, are comparatively recent developments. The subject was probably originally opened about 1880 by the pioneer work of Hill and Claus, who used ammonia liquor for washing hydrogen sulfide from the gas and regenerated the liquor by heat. The work of Feld in the first years of the present century was followed later by many investigators. As a result a number of liquid puri-

fication processes are now in commercial operation.

PROCESSES FOR HYDROGEN SULFIDE REMOVAL

CLASSIFICATION

In general, modern processes for the removal of hydrogen sulfide from coal gas can be classified in the following groups:

1. Dry processes.
   - (a) Oxidation to sulfur at ordinary temperatures.
   - (b) Oxidation to sulfur at elevated temperatures.
   - (c) Oxidation to sulfur oxides at elevated temperatures.
2. Liquid processes.
   - (a) Oxidation to sulfur or to thiosulfate or both.
   - (b) Absorption by a hydrogen sulfide solvent and desorption of the hydrogen sulfide.
   - (c) Absorption and fixation of the absorbed hydrogen sulfide with sulfur dioxide and ammonia.
   - (d) Absorption and disposal or utilization of the solution.

The ordinary iron oxide process, or "dry box" process, is here classified in the group 1a. To be useful practically, the iron oxide must exhibit simultaneously the dual function of absorbing the hydrogen sulfide and oxidation to sulfur. Methods included in the groups 1b and 1c are ordinarily catalytical processes at higher temperatures. For such methods the gas must be heated, and an efficient gas heat-exchanger is considered essential for practical economic operation. No classification under dry processes is included for adsorption of hydrogen sulfide by solids, followed by desorption of the hydrogen sulfide. Such processes are within the realm of possibility, but the common adsorbents function also as oxidation catalysts, and, practically, the adsorbed hydrogen sulfide is oxidized before it can be desorbed.

For liquid processes, a liquid having a hydrogen sulfide-absorbing power much greater than that of water is a practical necessity; otherwise, the necessary volume of scrubbing liquid is prohibitively large. Enhanced absorbing power for hydrogen sulfide is usually obtained in either of two ways: (a) by using a solution of sufficient alkalinity, or, technically, of sufficiently high pH, so that a major part of the absorbed hydrogen sulfide is held as a hydrosulfide; or (b) by using an ingredient in the solution that combines with the hydrogen sulfide to form other compounds. The chemical nature of the solution, of course, must be such that the regenerative step that follows is operative.

PROCESSES FOR OXIDATION TO SULFUR AT ORDINARY TEMPERATURES

Iron Oxide Processes. The classic dry iron oxide method for combined hydrogen sulfide absorption and oxidation to elemental sulfur was developed for practical use in the 1860's and is still in almost general use. In this process, the gas is merely passed through beds of a loose material, such as wood shavings, mixed with an active iron oxide. The iron oxide absorbs hydrogen sulfide, probably forming some intermediate iron oxysulfide, and the intermediate compound absorbs oxygen to form sulfur. For this process, the gas must contain sufficient oxygen for the oxidation and to provide a high enough oxygen concentration to obtain a sufficiently rapid oxidation. To provide the necessary amount of oxygen, it is general practice to add the proper amount of air to the gas. The rate of oxygen absorption becomes slower when the oxygen concentration in the gas is lower. This makes it impossible to utilize all the oxygen in the gas. Commercial-sized purifier boxes are able to utilize the

oxygen until the oxygen content of the gas is reduced to 0.4 [56, 57] to 0.6 percent.[58]

Recent advances in gas purification by the iron oxide box process have included: (1) correlation of sizes and capacities of existing equipment in order to ascertain the most efficient design; (2) studies of the effects of temperature, humidity, pH control, hydrocyanic acid and incidental hydrocyanic acid removal, the addition of air to gas, and the manner of rotation of boxes on the operating results of iron oxide boxes; (3) studies of the variations in activities of iron oxides produced and treated in different manners, and production of oxides having greater activity; (4) improved techniques for testing iron oxides and for more reliable laboratory evaluation of oxides; (5) modification of oxide box techniques to facilitate sulfur extraction from spent oxide, and methods for sulfur extraction; (6) adaptation of iron oxide boxes for purifying gases under higher pressures; and (7) development of the Thyssen-Lenze towers for oxide purification.

Oxide boxes are ordinarily boxes of large horizontal cross-sectional area and relatively low height, usually not over 10 or 15 feet. Inside the boxes are horizontal latticelike supports, each support holding one layer of iron oxide purifying material. The depth of each layer is usually between 3 and 6 feet, and two or more layers are commonly placed in each box. Figure 1 shows a group of four iron oxide purifier boxes at Indianapolis, Ind. The lifting equipment for removing the top plate from a box can be seen above the farthest box.

The coal gas to be purified is admitted in the top of the box and passes downward through the layers and out the bottom, or it is admitted in the bottom and passes up through the layers and out the top. A number of boxes are placed in series so that the gas passes through four to eight or more layers of purifying material, depending usually upon the hydrogen sulfide content of the gas and upon the urgency of maintaining continuous efficient hydrogen sulfide removal.

Two or more purifier boxes in series are usually connected with a system of valve and gas-piping connections to permit changing either the direction of gas flow through the boxes, from upward flow to downward flow, or the order of the boxes in the series. For example, an installation with four purifier boxes are connected so that the gas first goes in series through box 1, then through 2, 3, and last through 4, abbreviated "1-2-3-4." Valves and connections are provided so that the gas flow can be changed so that it passes through the series in any of the following orders, 4-1-2-3, 3-4-1-2, and 2-3-4-1. Also, it is sometimes arranged that the last two boxes in the series can be interchanged without affecting the order of preceding boxes. The practice of changing the order of the boxes in the series is commonly termed "rotation of boxes."

The purifying material is usually a mixture of a loose material such as wood shavings or crushed blast-furnace slag with a chemically active form of hydrated iron oxide. The iron oxides are prepared from rusted iron borings or from iron salts, or from hydrous iron ores—the so-called bog ores—or they are recovered from chemical manufacturing processes.

In the operation of the dry box, the sulfur formed by the absorption of hydrogen sulfide and oxygen accumulates in the layers of purifying material. Because the

[56] Schobel, C. O., *Proc. Am. Gas Assoc.*, **1931**, 1065 7.

[57] Seil, G. E., Heiligman, H. A., and Clark, T. H., *Am. Gas J.*, **130**, No. 5, 39–42, No. 6, 32–8 (1929).

[58] Clayton, R. H., Avery, H. B., and Taylor, H. F., *Gas J.*, **220**, 937–9 (1937).
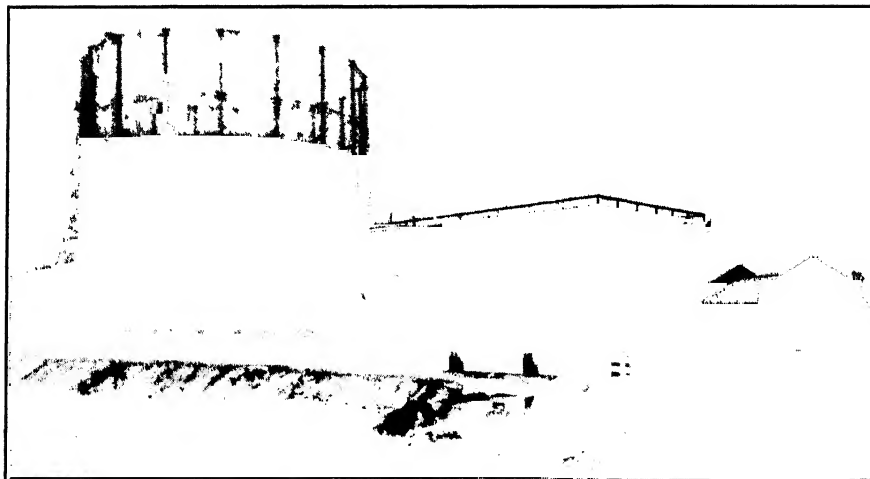
FIG. 1   Iron oxide purifier boxes at Indianapolis Ind

rates of absorption of hydrogen sulfide and oxygen by the dry purifying material are slow, the gas velocity must be slow   Ordinarily, gas velocities, calculated as gas volume per hour divided by the square feet of cross-sectional area, are in the range from 80 to 190 cubic feet per hour per square foot of horizontal section   Since this is a very slow gas velocity, purifier box installations must have a large horizontal cross-sectional area and require a large ground space   Where available ground space is limited, this consideration alone may require the adoption of other processes for hydrogen sulfide removal

The size of equipment in American practice is usually in accordance with the well-known Steere formula,

Cubic feet of gas per hour

$$= \frac{3,000 \times A(D + C)}{S}$$

in which A is the horizontal cross-sectional area of one dry box in square feet and is

calculated on the basis of the allowable gas velocity, which is usually around 100 cubic feet of gas per hour per square foot of horizontal cross-section area, D is the total depth of purifying material through which the gas travels before leaving the series of purifier boxes, C is a factor depending on the number of boxes in series, being 4 for a two-box series, 8 for a three-box series, and 10 for a four-box series, and S is a factor depending on the hydrogen sulfide content of the coal gas according to the following table

GRAINS OF HYDROGEN SULFIDE PER 100 CUBIC FEET IN GAS	FACTOR S
1,000 or more	720
900	700
800	675
700	640
600	600
500	560
400	525
300	500
200 or less	480

The use of the Steere formula and other rules for the design of purifier boxes is discussed more fully and critically in reference books on the subject.[4, 59]

European practice in purifier box design differs somewhat from American practice. Since both are based on practical operating experience, they do not differ materially. The apparent difference is mainly due to the method of applying safety factors. American practice seems to provide for an anticipated future gas rate, and Meade recommended a more liberal design because of the possibility of future expansion. For a more detailed study of the design and operation of purifier boxes, reference should be made to various published articles.[60, 61]

With any given purifier box installation, it is desirable to operate as long as possible before replacing the purifying material. Various conditions that are subject to control during this period of operation are: (1) temperature of the gas and the purifier boxes; (2) humidity of the gas; (3) acidity or pH of the purifying material; (4) addition of air or oxygen; and (5) manner of rotation of boxes.

Continued study of the chemistry of the iron oxide purification process and of the results of tests during practical operation have continued to throw light on the subject and have made improved control possible.

Lower temperatures in general cause chemical reactions to be slower. It is necessary to maintain the temperature in the purifier boxes sufficiently to obtain the desired purification efficiency. This is especially true when the accumulation of sulfur in the purifying material is showing its effect in retarding efficiency. Temperatures of 100° F to 120° F are considered desirable, especially in purifier boxes after the first box in the series.[62, 63] Operation at higher temperatures, though theoretically advantageous, is not safe because such temperatures may be the result of local overheating which destroys the desirable physical characteristics of the purifying material. Schobel mentioned 120° F as a maximum safe outlet temperature for purifier boxes.[56]

Humidity and its relation to purifier-box operation are also important. Purifier-box capacity is impaired by both too high and too low humidities. A humidity of 65 percent at 100° F has been reported as the optimum condition.[64] Higher humidities cause the water content of the purifying material to become so high that the material gets soggy and packs. The water content of the purifying material should be kept around 50 percent for highest capacity.[65] Special apparatus can be used for the control of both temperature and humidity.[66]

Alkalinity control or pH control is necessary if the purifying material is to be kept in the best condition. The purifying material will become acidic in use unless the condition is kept corrected. It is com-

[59] Morgan, J. J., *Textbook of American Gas Practice*, J. J. Morgan, Maplewood, N. J., 2nd ed., 1931, Vol. I, 969 pp. Pacific Const Gas Association, *Gas Engineers' Handbook*, McGraw-Hill Book Co., New York, 1934, 1017 pp.

[60] Offe, G., *Gas- u. Wasserfach*, **71**, 222–4 (1928). Pearson, G. C., *Gas J.*, **186**, 797–807 (1929). Anon., *Gas J.*, **202**, 922–4 (1933), **203**, 51–2 (1933). Zweig, W., and Kossendey, F., *Gas- u. Wasserfach*, **76**, 644-8 (1933). Anon., *Gas World*, **100**, 447–52 (1934). Marshall, J. R., *ibid.*, **102**, 58–60 (1935), **103**, 74–6 (1935). Pickard, K., *Gas J.*, **222**, 121–3 (1938).

[61] Sweeney, E. L., *Am. Gas J.*, **150**, No. 6, 39–42, 44–7 (1939).

[62] Pott, A., Broche, H., and Thomas, H., *Gluckauf*, **69**, 1158–9 (1933).

[63] Broche, H., U. S. Pat. 2,007,741 (1935).

[64] Huff, W. J., and Milbourne, C. G., *Proc. Am. Gas Assoc.*, **1930**, 856–86.

[65] Brückner, H., *Brennstoff-Chem.*, **17**, 21–3 (1936).

[66] W. C. Holmes and Co., Mitchell, G. P., and Keillor, G. E. H., Brit. Pat. 483,758 (1938).

mon practice to mix some lime with the original purifying material before it is placed in the purifier box, especially if the original iron oxide contains humic acid, as some bog ores do, or other acidic materials. At lower pH's, there is a tendency for the active iron compounds to revert to less active ones. The rate of hydrogen sulfide absorption is also lower at lower pH's, although the rate of oxygen absorption is not much affected.[67] It is common to permit sufficient ammonia gas to enter the boxes to maintain the pH at about 7.0. This practice has been described by Sweeney[61] and Murphy[68] and in books which have been referred to previously.

Adding air to gas may be necessary when the gas as produced does not contain enough oxygen to oxidize the hydrogen sulfide. It is practically impossible in gas-making processes to exclude all air. The amount of oxygen in the gas produced normally depends upon the care taken to prevent air admixture, upon the condition of the retorts or coke ovens, and upon the pressures inside the coke chambers and flues.

Adequate attention should be given to the oxygen content of gas inasmuch as that factor is of major importance for the proper performance of purifier boxes.[58] Only that oxygen in the gas above about 0.4 percent is available for oxidation in the purifying material,[56, 57, 58] and it is necessary to have sufficient oxygen present above this concentration. Hydrogen sulfide requires for its oxidation one-half of its volume of oxygen. Thus, if the gas to be purified contains 638 grains of hydrogen sulfide per 100 cubic feet, or 1 percent by volume, the oxygen content required in the

inlet gas will need to be the sum of 0.5 percent required for oxidation and 0.4 percent, below which level oxygen is practically unavailable, or a total of 0.9 percent oxygen. Actually, still higher oxygen contents in the gas increase the capacity of purifier boxes, since the capacity of the boxes is usually limited by the rate at which they can absorb oxygen, and not by the rate at which they can absorb hydrogen sulfide. Within practical limits, the use of additional air can be resorted to in order to maintain purifier-box capacity when other means of control are not sufficiently effective. Adding greater quantities of air to the gas, of course, dilutes the gas and may aggravate gum troubles, both of which must be considered.

With, say, four oxide boxes in series, the first box is working on gas containing the full hydrogen sulfide content. Absorption of hydrogen sulfide occurs more rapidly than absorption of oxygen. Under such conditions, the iron oxide becomes highly fouled to iron sulfide—an especially undesirable condition because it causes reversion of the iron to less active forms. If such a box that is becoming highly fouled is placed at the final end of the series where only traces of hydrogen sulfide are in the gas, it can absorb oxygen from the gas without absorbing material quantities of hydrogen sulfide. Gradual oxidation will occur, and the purifying material becomes revivified. Changing the order of the purifier boxes in the series at regular intervals, as mentioned previously, is commonly practiced in order to distribute the sulfur load evenly among the boxes as well as to maintain the purifying material in a partially sulfided and active form.

If for some reason a purifier box becomes highly fouled and cannot be revivified by the normal practice of rotation, it is necessary to revivify the purifying

[67] Bunte, K., *Gas- u. Wasserfach,* **78,** 954–9 (1935).

[68] Murphy, E. J., *Proc. Am. Gas Assoc.,* **1935,** 701–2.

material by other means. This can be done by actually removing the purifying material from the box and storing it in the open air until it becomes revivified. The fouled purifying material must be watched carefully at such times because it often ignites by spontaneous combustion. More recently, revivification *in situ* is becoming more common, although it is necessary sometimes to revivify in the old manner occasionally to break up dense zones of solid deposits in the purifying material. Revivification *in situ* is accomplished by recirculating the same gas continuously through the box, meanwhile carefully admitting enough air for slow oxidation. This practice should be accompanied by careful supervision, because revivification generates heat and too rapid revivification will fuse the sulfur and actually produce fires within the purifying material. There is, also the possibility of explosion if the admixture of air gets very badly out of control. Revivification *in situ* does avoid the laborious task of replacing purifier material in the large purifier boxes, and also it avoids the odor nuisance and fire hazards of revivifying in the open air.

Chemical and physical examinations of iron oxides have been made with a twofold purpose. One is to aid the gas manufacturer in the selection and use of the most desirable oxide; the other, to aid in the manufacture and preparation of suitable oxides. There are various empirical tests to measure the rate and amount of hydrogen sulfide absorption by the sample of iron oxide, and tests for measuring the rates of regeneration. Ordinarily, to be sufficiently rapid, a test should be kept relatively simple; but to be of most practical value, it should duplicate the conditions encountered in actual use, so that it becomes difficult and complicated. In practical use of the oxide in a purifier box,

its behavior while simultaneously absorbing hydrogen sulfide and oxygen is of most importance. The various methods that have been proposed for making tests indicating the activity of iron oxides [11, 56, 65, 69] duplicate some plant conditions closely, but it is desirable that practical operating data be correlated with the results of laboratory tests.

Desirable characteristics of a good oxide have been listed by Brückner [70] and by Dotterweich and Huff.[71] A desirable oxide should be friable and easily crumbled, not claylike, and its particles should be of microscopic size. Natural oxides should be reasonably free from roots and other organic matter and humic acids. Acids, of course, should be neutralized by a thorough mixing with soda ash or lime before the oxide is used. Huff called attention to the greater chemical activity of oxides of colloidal size and also some beneficial effects of alumina. It has been proposed to improve iron oxide by adding small amounts of compounds of copper, mercury, and lead,[72] by admixing active carbon in various manners,[73] and by heat treatment with wet soda ash.[74] The manner of rusting iron borings can be altered to make a superior oxide.[75] At one time a byproduct of the bleaching industry containing manganese dioxide known as Weldon mud was available, and this material to some extent

[69] Dunkley, W. A., and Leitch, R. D., *U. S. Bur. Mines, Tech. Paper* **332** (1924), 33 pp. Currie, W. A., Jr., *Gas World,* **99,** 553–7 (1933). Bunte, K., Brückner, H., and Leuze, A., *Gas- u. Wasserfach,* **79,** 669–72, 689–93 (1936).

[70] Brückner, H., *ibid.,* **81,** 822–8 (1938).

[71] Dotterweich, F., and Huff, W. J., *Gas Age,* **82,** 43–4. 54, 56–8 (1938).

[72] Bolling. E. H., Brit. Pat. 454,175 (1936).

[73] Olin, H., Scarth, V., and Starkweather, W., *Gas Age-Record,* **70,** 561–4 (1932). Carbonisation et Charbons Actifs, Brit. Pat. **479,410** (1938). Hene, E., Brit. Pat. **498,734** (1939).

[74] Ruhrchemie A.-G., Ger. Pat. **659,407** (1938).

[75] Smyly, A. L., U. S. Pat. **2,045,807** (1936).

replaced iron oxide as purifier. Manganese dioxide had acquired a reputation as a superior, highly active material, especially suitable for removing the final traces of hydrogen sulfide from the gas. Special purifying materials containing manganese have been made, but, because of the relatively low cost of iron oxides, the use of manganese does not seem justified except under certain special situations.

When wood shavings are mixed with the purifying material, certain types of bacteria can thrive inside the purifier box while it is in use. Some types of bacteria can regenerate hydrogen sulfide from sulfur and introduce traces into purified gas, and others can also cause caking in the bed of purifying material.[76] Copper sulfate and other bactericides have been proposed as preventives.

Other ingredients in coal gas, notably tar, naphthalene, and hydrocyanic acid, have effects on gas purification in iron oxide dry boxes. The effect of tar and naphthalene is mainly physical. They coat the active iron surfaces with oily layers which prevent the purifying action, and their accumulation restricts the gas flow and causes high back pressures. Hydrocyanic acid has a detrimental chemical effect. It usually combines with the iron to produce complex iron cyanides of little or no activity for removing hydrogen sulfide. Ordinarily, a set of purifier boxes removes somewhat more than half of the hydrocyanic acid from the gas, and the amount removed is greater when greater amounts of ammonia are used to keep the purifying material alkaline.[77]

If coal gas contains nitric oxide, of importance in connection with the formation of gums in the gas-distribution system, nitric oxide is absorbed as well as hydrogen sulfide in zones where iron sulfide is being formed faster than it is being oxidized. Nitric oxide can be again released to the gas when revivification of the iron sulfide occurs. It is possible to operate purifier boxes in a prescribed manner so as to absorb nitric oxide from the gas and to avoid subsequently releasing it back into the gas.[78]

The conventional iron oxide dry box has disadvantages due to its large size and ground-space requirement and because of the length of time and amount of labor required for changing oxide. Some attempts have been made to design equipment for this process that is more compact and continuous in operation.[79] As far as known, these modifications have not been adopted.

Thyssen-Lenze Tower Purifiers. Another modification in design of equipment for the dry iron oxide process is known as Thyssen-Lenze tower purifiers; these purifiers are in use in a number of European gas plants. They are designed so as to require much less ground space and also so that the purifying material can be replaced in a shorter time. Installations at Aldorf, near Aachen, and Duisburg-Hamborn, in Germany have been described by Lenze,[80] and the first English installation at Wandsworth has been described by Croft,[81] together with an account of results during about six months of operation.

An installation to purify gas with the Thyssen-Lenze tower system consists of a

76 Anderson, G. W., *Gas World*, **91**, 54–5 (1929). Thorne, W. F., *Gas J.*, **209**, 370 (1935).
77 Downing, R. C., *Proc. Am. Gas Assoc.*, **1936**, 699–702.

78 Ward, A. L., and Jordan, C. W., U. S. Pat. 2,073,083 (1937).
79 Thau, A., *Gas Age-Record*, **57**, 461 (1926). Brady, E. J., U. S. Pat. 1,731,223 (1929).
80 Lenze, F., and Borchardt, A., *Gas- u. Wasserfach*, **74**, 445 9 (1931).
81 Croft, C. M., *Inst. Gas Engrs.*, *Commun.* **212** (1939), 17 pp.

number of tall circular towers, with gas connections and valves such that the gas can be directed in series through the towers and the sequence can be altered or "rotated" in the same manner as with series of purifier boxes. A vertical section through a tower purifier is shown in Fig. 2, in which the general construction of these towers is evident. Each tower contains a number of specially constructed baskets, placed one on top of another, each containing either two or four layers of purifying material. In this illustration, two layers are shown. The center of each basket consists of a vertical tube, and when the baskets are in place they form a central vertical tubular continuation of the inlet gas line. There are openings in each of these vertical tubular sections so that the inlet gas can enter between each pair of oxide layers. Part of this gas goes upward through one of the layers, and the rest goes downward through the other layer. After leaving the oxide, the gas passes through openings between the outside rims of the baskets and enters the annular space between the outside of the baskets and the wall of the tower itself. The gas outlet nozzle connects into this annular space and is in the side of the tower about half way between the top and the bottom.

To install and to remove the baskets, a movable crane is provided. The crane is located so that it can be moved into position to work on any one of the towers. The spare sets of baskets provided should be kept full of fresh oxide so that they will be ready for use whenever necessary. In order to change purifying material in a tower, all that needs to be done is to bypass the gas around the tower and shut the inlet and outlet gas valves, purge the tower, remove the top plate of the tower, remove and replace the baskets with the crane, and close and purge the tower. Croft[81] re-

ported that in practice, 6¼ hours is required to change a 22-foot-diameter tower, not allowing time for the final purge. To include the final purge, an additional 1½ hours should be added, making a total of 7¾ hours.

In practice, the gas flow through the series of towers is handled in the same
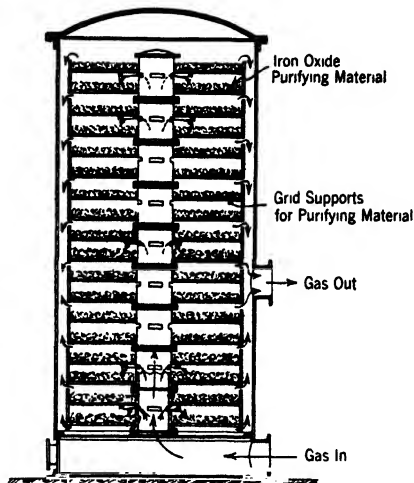
FIG. 2. Thyssen-Lenze purifier tower.

manner as with a series of purifier boxes. Also, it is anticipated that, with a tower designed as above, the sulfur can be extracted from the spent oxide *in situ*.[82]

Still another type of tower purifier has been described by Thau.[83] In this type, porous briquets of purifying material were used. Some of these purifying briquets were removed from time to time from the bottom of the tower by a special cell valve, and fresh briquets were added to the top of the tower through a conventional double-bell feeding arrangement. In this

82 Thyssen'sche Gas- u. Wasserwerke G.m.b.H., Brit. Pat. 345,880 (1930).
83 Thau, A., *Gas- u. Wasserfach*, **77**, 33–5 (1934); *Colliery Guardian*, **148**, 151–3 (1934).

manner, the purifying briquets gradually descended to the bottom of the tower and were removed. Sulfur was extracted from the spent briquets, and the briquets were again fed to the top of the tower. The statement was made later that this development was tried on a pilot-plant scale, but was abandoned.[84]

Purification of Gas under Pressure. Purifier boxes adapted for hydrogen sulfide removal from gases at 190 pounds per square inch pressure were built in the Saar district in Germany for the purification of 6 million cubic feet of gas per day. A description of this installation with photographs and drawings of the equipment has been published by Thau.[84] When hydrogen sulfide is to be removed from compressed gases, a method frequently used is to wash the gas with water in a packed tower.[85]

Recovery of Sulfur from Spent Oxide. Sulfur may be recovered from the spent purifying material or "spent oxide" when its recovery is economical. The three methods for effecting this recovery are: (1) roasting the spent oxide to form sulfur dioxide, usually for sulfuric acid production; (2) extraction of the sulfur with some solvent; and (3) distillation of the sulfur from the spent oxide.

Roasting and making sulfuric acid is the original method and probably still the most common one. When this process is to be applied to the spent oxide, it is desirable that a noncombustible carrier be substituted for wood shavings for mixing the original purifying material. Also, a porous, granular iron oxide is satisfactory without a carrier. The operation of purifier boxes when crushed blast-furnace slag

serves as a carrier,[86] and the use of spent oxide for sulfuric acid manufacture,[87] have been described. The ignited residue remaining after roasting is worthless as a gas-purifying material.[88]

Sulfur has been extracted with the following solvents: (*a*) ammonium sulfide solution; and (*b*) organic liquids such as carbon disulfide, hydrocarbon oils, and halogenated hydrocarbon solvents. Ammonium sulfide and ordinary organic solvents have long been known as solvents for sulfur. Patentable developments have been confined to special manners for their use, and to exceptional properties of solvents that have been developed more recently. In general, the use of ammonium sulfide may require prolonged extraction and the expenditure of more heat, because tarry impurities retard extraction by aqueous solutions. Carbon disulfide and organic liquids will ordinarily extract both tar and sulfur, and the tar will contaminate the sulfur. Obviously, tar is much more soluble than sulfur, and a preliminary extraction with less solvent which will remove the tar can be followed by the regular extraction to recover the sulfur. Various techniques have been developed for conducting this extraction and for the purification of the resulting sulfur.[89]

The distillation of sulfur from spent oxide leaves a residue containing about 15

84 Thau, A., *Gas World*, **109**, Coking Sect., 115–8 (1938).

85 Gesellschaft für Linde's Eismachinen A.-G., Brit. Pat. 286,622 (1927). Korobchanskii, I. E., *Chimie & industrie*, **29**, 1057 (1932).

86 Presbrey, R. L., *Am. Gas Assoc.*, **1936**, 698. Sweeney, E. L., *ibid.*, **1936**, 696–8.

87 Ibbotson, W. H., *Ind Chemist*, **4**, 513–21 (1928).

88 Sweeney, E. L., and Sands, A. E., *Gas Age-Record*, **77**, 657–62 (1936).

89 Giller, F., and I. G. Farbenindustrie A.-G., Ger. Pats. 565,538 (1930), 590,173 (1933), 637,-445 (1936); Brit. Pat. 449,911 (1936). Bordo, J. A., U. S. Pat. 1,962,051 (1934). Ragg, W. G., and Well, J. A., Brit. Pat. 414,074 (1934). Clayton, R. H., Williams, H. E., and Avery, H. B., U. S. Pat. 2,040,359 (1936). DuPont, F. E., U. S. Pat. 2,088,190 (1937). Beattie, R. W., U. S. Pat. 2,118,140 (1938).

percent of the sulfur in the form of iron sulfide.[90] Different techniques for carrying out this distillation and recovery of sulfur from spent oxide include the use of steam,[91] and distillation *in situ* by heating a small part of the gas and passing it through the oxide box.[92] Methods of preparing iron oxide purifying materials to withstand distillation processes without losing their value for subsequent use have been studied.[93]

Activated carbon[94, 95] *and silica gel*[96] can be used as purifying material instead of iron oxide to remove hydrogen sulfide from gases. Sufficient oxygen must also be present in the gas, and these compounds catalyze the oxidation of the hydrogen sulfide to sulfur. The sulfur remains as a solid deposit within the catalyst. After the sulfur accumulates to an extent that interferes with the gas flow, the entire mass is treated to remove the sulfur, and the carbon or the silica gel is ready for reuse. Experimental plants have been operated in which coal gas is purified by activated carbon.[94] For practical operation, about 13 grains of ammonia per 100 cubic feet must be present for proper functioning of the carbon catalyst, and certain hydrocarbons that would polymerize within the catalyst must be absent. To avoid the troubles due to such hydrocarbons, additional equipment has been necessary for preliminary purification of the gas. The operation be-

came rather complicated, and as a result this process has not been commercialized [53, 97] for coal gas. For the purification of blue water-gas and producer gas used in high-pressure synthetic processes, however, it is in operation on a large scale.

OXIDATION OF HYDROGEN SULFIDE TO SULFUR OR TO SULFUR DIOXIDE AT ELEVATED TEMPERATURES

Because of the difficulty with the activated-carbon process at ordinary temperatures due to polymerization of hydrocarbons and inactivation of the catalyst, this process has been studied at higher temperatures. It has been claimed that at 350° C, or above, this troublesome polymerization is avoided.[98] Also, at these higher temperatures, there is a tendency to oxidize the hydrogen sulfide to sulfur dioxide. In fact, practical developments in this direction attempt to convert all the hydrogen sulfide to sulfur dioxide and to recover the sulfur dioxide in some manner.[99] In the newer "Katasulf" process, the hydrogen sulfide is oxidized to sulfur dioxide. However, this step is followed by a liquid washing process in order finally to recover both ammonia and sulfur as ammonium sulfate. For this reason this process is discussed later under simultaneous hydrogen sulfide and ammonia recovery as ammonium salts.

Another process to remove and convert hydrogen sulfide to sulfur dioxide was developed by Houdry.[100] It is carried out in two steps. The gas is first heated to

[90] Gluud, W., *Brennstoff-Chem.*, **8**, 168-9 (1927).

[91] Bollmann, H., and Engelmann, W., U. S. Pat. 1,925,027 (1933).

[92] Zahn and Co., G.m.b.H., Fr. Pat. 749,495 (1933).

[93] Raffluer, E., U. S. Pat. 1,900,667 (1933).

[94] Engelhardt, A., *Gas- u. Wasserfach*, **71**, 290-7 (1928); *Glückauf*, **73**, 925-33 (1937).

[95] I. G. Farbenindustrie A.-G., Brit. Pats. 267,018, 282,508 (1926); U. S. Pat. 1,984,971 (1934). Committee on Gas Manufacture, *Gas J.*, **184**, 526-7 (1928).

[96] Miller, E. B., and Connolly, G. C., Brit. Pat. 280,947 (1926); U. S. Pat. 1,895,724 (1933).

[97] Todd, E. W., *Proc. Trans. Nova Scotian Inst. Sci.*, **17**, Pt. 2, 12-3 (1928).

[98] Dreyer, K., Brit. Pat. 473,248 (1937).

[99] Bähr, H., *Gas- u. Wasserfach*, **71**, 169-73 (1928); U. S. Pat. 1,678,630 (1928); *Chem. Fabrik*, **11**, 10-20 (1938); U. S. Pat. 2,152,454 (1939). Wietzel, G., Jannick, J., and Fried, F., U. S. Pat. 1,782,590 (1931).

[100] Houdry, E., Burt, W. F., Pew, A. E., Jr., and Peters, W. A., Jr., *Natl. Petroleum News*, **30**, R-570-80 (1938).

400° C and passed through a chamber containing nickel oxide supported on a porous carrier. In this step, hydrogen sulfide is removed from the gas to form nickel sulfide. The chamber holding the nickel sulfide is then removed from the gas circulation and is regenerated by a stream of air. The air oxidizes the nickel sulfide to sulfur dioxide and nickel oxide. The chamber now containing nickel oxide can be used again for the first step to remove hydrogen sulfide. For this process it is necessary to have a number of chambers in service so that a chamber of regenerated material is always available when necessary. A pilot plant has been operated on this process, but no commercial installations have been reported.[100]

LIQUID PROCESSES FOR OXIDATION OF HYDROGEN SULFIDE TO SULFUR

Liquid processes for hydrogen sulfide removal have been developed in an attempt to avoid certain drawbacks of the dry processes. The iron oxide purifier-box process previously described is simple and reliable in its operation and is admirably suited to small coal-gas plants. The amount of ground space required, the irregular need of labor for emptying and recharging the large boxes, and the low value of the recovered sulfur are the principal disadvantages. Often, when plant expansions are contemplated, insufficient ground space is available for enlargement of the iron oxide purifier boxes. Several processes utilizing liquids for removing hydrogen sulfide have been developed and are employed commercially.

Probably the earliest liquid process after the original milk-of-lime purifiers was that of Hill and Claus in 1880, who attempted to remove hydrogen sulfide by means of ammonia liquor in a commercial process. The early work of Feld and Burkheiser is

well known. Feld attempted to evolve a practical scheme for converting the hydrogen sulfide and ammonia to ammonium sulfate, and his work included an extensive study of hydrogen sulfide absorption by polythionates and regeneration of the polythionates with sulfur dioxide. The Feld process, applying the above reactions, has been described in detail by Wagner;[101] it can be employed to recover hydrogen sulfide as elemental sulfur and also to recover the hydrogen sulfide and ammonia simultaneously as ammonium sulfate. Though in commercial operation for a number of years, the process was abandoned in favor of other methods. Burkheiser attempted to recover ammonia as ammonium sulfite by means of sulfur dioxide obtained from the sulfur produced by removing hydrogen sulfide. He used a suspension of iron oxide in a liquid process to remove the hydrogen sulfide and obtain the sulfur.[102] The work of Feld and Burkheiser was done in the early years of this century. Since this pioneer work, many others have worked upon the subject.

In the first step of Burkheiser's process, as above mentioned, a suspension of iron oxide was used to scrub hydrogen sulfide from the gas, and the iron sulfide was oxidized by air to obtain elemental sulfur. The removal of hydrogen sulfide by such suspensions is very slow. Later work resulted in the development of methods employing suspensions in alkaline solutions, and of improved equipment to oxidize the solution to form sulfur and to separate the free sulfur by flotation. Such processes can use either iron or nickel compounds with alkaline solution.

101 Wagner, F. H., *Coal Gas Residuals*, McGraw-Hill Book Co., New York, 2nd ed., 1918, 214 pp.
102 Reichel, J., *Stahl u. Eisen*, **33**, 982–7 (1913).

The Ferrox Sulfur-Recovery and the Nickel Sulfur-Recovery Processes. The use of iron suspensions in alkaline solutions has been developed commercially and is known as the ferrox sulfur-recovery process; the method employing nickel is known as the nickel sulfur-recovery process. The iron method was developed independently and simultaneously in the United States [103, 104] and in Germany.[105] In the United States, soda ash solutions were favored, instead of

of soda ash containing iron oxide in suspension is pumped over a countercurrent gas scrubber packed with wooden hurdles. The solution absorbs hydrogen sulfide from the gas, mainly to form hydrosulfide from the sodium carbonate in the solution:

$$Na_2CO_3 + H_2S = NaHS + NaHCO_3$$
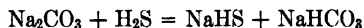
and to a minor extent to form iron sulfide from part of the suspended iron oxide:

$$Fe_2O_3(H_2O)_x + 3H_2S = Fe_2S_3(H_2O)_x + 3H_2O$$
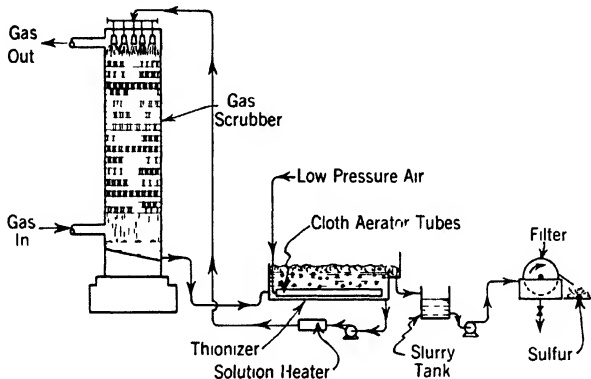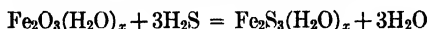
Fig. 3   Flow diagram of the Koppers ferrox liquid purification process.

the ammoniacal suspensions used in Germany.

A number of commercial units were built in the United States and a couple in Germany.[103, 106]   A flow diagram of the United States process is shown in Fig. 3; it applies to both the ferrox and nickel processes, the only difference being the chemical composition of the solution.   In the ferrox process, a weakly alkaline solution

103 Sperr, F. W., Jr., *Proc. Can. Gas Assoc.*, 1926, 224–65; *Gas Age-Record*, **58**, 73–6, 80 (1926).
104 Mann, M. D., Jr., and Lebo, R. B., U. S. Pat. 1,525,140 (1925).
105 Gluud, W., and Schönfelder, R., *Chem. & Met. Eng.*, **34**, 742–3 (1927).
106 Ferbers, *Gas- u. Wasserfach*, **71**, 1133–7 (1928).   Gluud, W., Klempt, W., and Brodkorb, F., *Brennstoff-Chem.*, **11**, 23–7 (1930).

The sulfided solution flows into an aerating tank containing submerged cloth-covered aerator tubes. Air pumped into the aerator tubes is finely dispersed and rises through the solution in the form of small bubbles. Baffles are placed in the aerating tank to prevent the inlet solution from mixing with regenerated solutions. By the time the solution leaves the outlet end of the tank, the hydrosulfides are oxidized. The solution is then pumped back to the gas scrubber. In the aerating tank, the hydrosulfide is oxidized mainly to sulfur:

$$NaHS + NaHCO_3 + \tfrac{1}{2}O_2$$
$$= Na_2CO_3 + H_2O + S$$
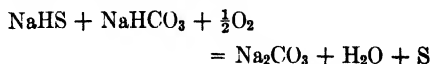
Secondary oxidation of the sulfur to sodium thiosulfate also occurs to some ex-

tent. The elemental sulfur is formed as a very finely divided precipitate and separates as a froth over the surface of the liquor in the aerating tank. As the quantity of sulfur accumulates, the thickness of the froth increases until it overflows into a sulfur-slurry collecting tank. From here it passes to filters and equipment to produce commercially desirable forms of sulfur.

For this process, when the wash liquor consists of a suspension of iron oxide in

FIG. 4. Flow diagram of Gluud's iron oxide liquid purification process.

ammonia liquor, Gluud used a tall narrow cylindrical tank full of the liquor as an aerating tank.[105] Figure 4 shows the flow in this system. Air from an air compressor passes continuously into the bottom of the tall aerating tank, 50 or more feet high. The solution to be oxidized flows into the bottom of this tank, and the oxidized solution overflows from the top. The sulfur is floated by the ascending air in the oxidizer and is skimmed from the top of the recirculating solution in much the same manner as with the shallow aerator tanks previously described. It may be noted that, in the process as developed by Gluud, the main differences from the original American practice were the use of (a) ammonia instead of soda ash to provide the alkalinity of the solution, (b) an enclosed aerating tank and equipment to recover ammonia

that would otherwise be lost in the air leaving the aerator, and (c) tall narrow aerator tanks instead of shallow ones, requiring a smaller volume of air but under a higher pressure.

In studying the early accounts of the ferrox or iron oxide process,[103, 105] it will be noted that the chemistry of the process is explained differently. In these earlier accounts, it was stated that the iron carries the hydrogen sulfide as iron sulfide. Actually, the amount of iron in suspension in the circulating liquor is far short of that required to carry the hydrogen sulfide. The iron does carry a minor amount of hydrogen sulfide, however, since it becomes sulfided in the foul solution and oxidized in the actified solution. The essential function of the iron is to form an oxygen carrier or oxidation catalyst that is not destroyed in the normal working of the process. Probably the active iron catalyst either is an intermediate iron-sulfur-oxygen compound, or in scrubbing coal gas containing hydrocyanic acid, may include some active iron cyanide compound.

The use of nickel compounds instead of iron occurred about the same time.[107] Unfortunately, nickel forms a soluble, catalytically inert compound with hydrocyanic acid, $Na_2Ni(CN)_4$; and nickel is a relatively expensive material. When more than 3 or 4 grains of hydrocyanic acid per 100 cubic feet are in the gas, the consumption of nickel to form this inert salt makes the cost of nickel prohibitive. Consequently, the nickel process has been restricted to the purification of gases of low hydrocyanic acid content and has not been used for coal gases.

107 Gluud, W., U. S. Pat. 1,597,964 (1926).
Morgen, R. A., Yard, W. S., and Rosenstein, L., Can. Pat. 263,221 (1926); U. S. Pat. 1,732,905 (1929). Cundall, K. N., *Chem. & Met. Eng.*, 34, 143–7 (1927).

In all the above processes, utilizing an alkaline liquid containing nickel or iron compounds as oxidation catalysts, part of the hydrogen sulfide is oxidized to thiosulfates. Also, any hydrocyanic acid that is in the gas is converted to thiocyanates, the formation of which consumes part of the sulfur. Thiosulfates and thiocyanates accordingly accumulate in the solution, and they must be removed in some manner. These liquors have found commercial application as weed-killers, and it is also possible to work up such solutions to recover pure thiosulfate and thiocyanate.

The amount of thiosulfate formation is affected by such operating conditions as temperature and alkalinity of solution. The process can also be operated to convert all the hydrogen sulfide to thiosulfate [108] if the conditions are such that this is economically more desirable.

Iron cyanide compounds that behave as oxygen carriers or oxidation catalysts have been briefly mentioned. Study on this subject has resulted in a technique of actually forming an active type of iron cyanide complex from ferrous sulfate before the iron compound is added to the circulating solution.[109] A process based on the above is known as the Pieters or the Staatsmijnen-Otto process. It is so operated that the hydrocyanic acid normally in the gas is used to transform further additions of ferrous sulfate to the desired iron cyanide complex. This process and its operation on a pilot-plant scale have been described by Pieters and others.[110]

[108] Sperr, F. W., Jr., U. S. Pat. 1,841,419 (1932).

[109] Pieters, H. A. J., U. S. Pat. 2,169,282 (1939).

[110] Smith, F. F., and Pryde, D. R., *Gas World*, **100**, Coking Sect., 44–6 (1934); *Chemistry & Industry*, **53**, 657–9 (1934). Pieters, H. A. J., *Chem. Eng. Congr., World Power Conf.*, 1936, No. C10, 12 pp.; *Brennstoff-Chem.*, **18**, 373–6 (1937).

Electrolytic oxidation has also been attempted for the regeneration of liquids for scrubbing hydrogen sulfide from gas. A process, as developed by Fischer,[111] uses an alkaline solution containing potassium ferrocyanide and ferricyanide. When gas is scrubbed with this solution, the ferricyanide oxidizes the hydrogen sulfide to sulfur and is itself reduced to ferrocyanide.

$$2K_3Fe(CN)_6 + H_2S + 2K_2CO_3$$
$$= 2K_4Fe(CN)_6 + 2KHCO_3 + S$$
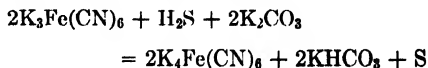
This reaction occurs in the gas scrubber, and, since sulfur has a pronounced tendency at the instant of formation to adhere to surfaces, a special mechanical washer is required to prevent stoppages from accumulated sulfur. Electrolytic oxidation compared to oxidation by air is relatively expensive. In this process sufficient electric energy is theoretically required to form ferricyanide and free hydrogen, not merely the smaller amount of energy needed to oxidize a hydrosulfide solution. However, the unusual purity and value of the sulfur produced have been claimed to offset the high electric power cost and to justify the process. An experimental installation was built and operated at the Hamburg, Germany, gasworks. Electric power consumption was reported to be about 1.8 kilowatt-hours per pound of sulfur, or about two times the theoretical.[112, 113] Because it is necessary to obtain a sulfur of an exceptional purity and value to justify the cost of electrolytic oxidation, the process has not been recommended for coal gases or other gases containing oily or tarry ingredients.[113]

Thylox Process for Sulfur Recovery. In the various preceding methods of scrubbing

[111] Fischer, F., U. S. Pat. 1,891,974 (1932).

[112] Müller, H., *Gas- u. Wasserfach*, **74**, 653–7 (1931).

[113] Thau, A., *Gas World*, **96**, 144–7 (1932).

hydrogen sulfide from gas with liquids and oxidizing the fouled liquor to form sulfur, alkaline solutions were employed to absorb and carry the hydrogen sulfide. The Thylox process [114] is different in that the solution contains an essentially neutral thioarsenate salt to carry the hydrogen sulfide. This salt absorbs and reacts with hydrogen sulfide to make a higher thioarsenate salt, that is, a thioarsenate in which more oxygen atoms have been replaced by sulfur. The higher thioarsenate salt can be oxidized by aeration; the oxidation produces elemental sulfur and converts the arsenic compound back to the original thioarsenate salt. The solution can then be used again for scrubbing hydrogen sulfide from the gas. The Thylox process has distinct advantages over the methods using alkaline solutions with iron and nickel compounds in that consumption of alkali to form thiosulfate is much reduced and the recovered sulfur is of higher purity. Because the Thylox process can be operated in the same equipment, prior installations that operated with the alkaline iron or nickel processes have been largely converted to the Thylox. The first commercial installation of the Thylox process was at Appleton, Wis., in 1926. All the more recently built sulfur-recovery plants have been designed for the Thylox process and are so operated.

The chemistry and the operation of the Thylox process have been variously described.[115]   To prepare the original solution, ordinary arsenic oxide and soda ash are dissolved in water in the proportion of two moles of soda ash to one mole of ar-

senic oxide. The resulting solution is a mixture of sodium carbonates, Na_2CO_3 and $NaHCO_3$, sodium arsenite, $NaAsO_2$, and arsenous acid, H_3AsO_3. Upon alternate absorptions of hydrogen sulfide from the gas and oxidations by aeration, sodium thioarsenites are formed and oxidized to thioarsenates and the carbon dioxide is expelled. The final oxidized solution contains sodium, arsenic, and sulfur in the proportions to form the compound Na_4-$As_2S_5O_2$. When gas containing hydrogen sulfide is scrubbed with this solution, one gram mole of hydrogen sulfide can readily be absorbed per two gram atoms of arsenic, as would be explained by the equation:

$$Na_4As_2S_5O_2 + H_2S = Na_4As_2S_6O + H_2O$$
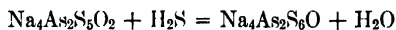
Actually, with more thorough contact and at higher temperatures of operation, an additional mole of hydrogen sulfide can be absorbed. However, this additional absorption is usually not obtained in practice. Upon aeration, sufficient oxygen can be absorbed to regenerate the original compound and liberate elemental sulfur, thus:

$$Na_4As_2S_6O + \tfrac{1}{2}O_2 = Na_4As_2S_5O_2 + S$$
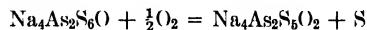
When additions of more arsenic are necessary to offset losses, solutions of arsenic oxide in water or in soda ash can be added. This freshly added arsenic is converted to the active thioarsenate form by a number of the alternate sulfidings and oxidations that occur in the normal operation of the process. Sodium thioarsenite, one of the intermediate compounds formed during the conversion of freshly added arsenic to active thioarsenate solution, is stable only at low concentrations at the pH of operating Thylox solutions, and it is important that additions of arsenic be made slowly.

114 Gollmar, H. A., U. S. Pats. 1,719,177, 1,719,762 (1929). Jacobson, D. L., U. S. Pat. 1,719,180 (1929).
115 Jacobson, D. L., *Gas Age-Record*, **63**, 597–600 (1929). Gollmar, H. A., *Ind. Eng. Chem.*, **26**, 130–2 (1934). Foxwell, G. E., and Grounds, A., *J. Inst. Fuel*, **12**, 281–8 (1939).

Otherwise decomposition and precipitation of some arsenic sulfide will occur.

A small part of the sulfur is oxidized further to soluble thiosulfates, as in the previously described sulfur-recovery processes. The tendency of hydrogen sulfide to be oxidized to thiosulfate is greater in the alkaline solutions of the earlier processes using soda ash or ammonia. In the essentially neutral Thylox solution, only around 10 to 15 percent of the sulfur forms thiosulfates as compared with 30 to 40 percent forming thiosulfates in the previously mentioned processes. Formation of sodium thiosulfate consumes soda ash and causes thiosulfate to accumulate in the solution.

Another part of the sulfur reacts with the hydrocyanic acid in the gas being scrubbed to form thiocyanates. The behavior of hydrocyanic acid is explained in a later paragraph. Sodium thiocyanate formation also consumes soda ash, but hydrocyanic acid removal from the gas is ordinarily considered worth more than the cost of the soda ash for its removal.

It is necessary, of course, that there be outlets for thiosulfate and thiocyanate to balance the rate of their formation. This is ordinarily done by removing sufficient volumes of the solution and adding water. If feasible, the solution removed can merely be discarded, or, if necessary, it can be acidified and filtered to recover its arsenic as arsenic sulfide before being discarded. Any arsenic sulfide so recovered is redissolved in soda ash and used to make subsequent arsenic additions to the purification system.

Although the above description and explanations have been on the basis of using soda ash and sodium salts in the Thylox process, they also apply in principle to the use of ammonia, the corresponding ammonium salts being formed. Coal gases, of course, contain ammonia, and sufficient ammonia can be added to the Thylox process from this source either by partially bypassing the ammonia-removal equipment or else by using concentrated ammonia liquor made from the ammonia still vapors. Most of the European installations have employed ammonia and have claimed reduced operating costs because of the lower equivalent value of ammonia.

The operation of the Thylox process is shown in the flow diagram, Fig. 5. The gas is scrubbed in a countercurrent tower packed ordinarily with wood hurdles. The solution passing therethrough absorbs hydrogen sulfide from the gas. Incidentally, the solution also absorbs any hydrocyanic acid that is in the gas, and this material is largely held merely by virtue of its physical solubility in aqueous solutions. From the bottom of the gas scrubber, the solution is pumped into tall aerating towers, called thionizers. Compressed air flows into the bottom of each thionizer and, in rising through the solution, oxidizes the sulfided thioarsenate and generates sulfur. Generating sulfur in the presence of hydrocyanic acid incidentally converts all that material to sodium thiocyanate. The rising air bubbles in the thionizers simultaneously entangle the elemental sulfur particles and cause them to rise to the top surface of the liquid in the form of a sulfur-bearing froth. The liquid level in the thionizer is maintained slightly lower than the level of a dam over which the sulfur-bearing froth overflows. The liquid leaving the top of the thionizer becomes regenerated during its upward flow through the thionizer. The regenerated solution then flows to the top of the gas scrubber for further hydrogen sulfide absorption.

Figures 6 and 7 show two commercial installations of the Thylox process. Figure 6 is at the plant of the Boston Consoli-
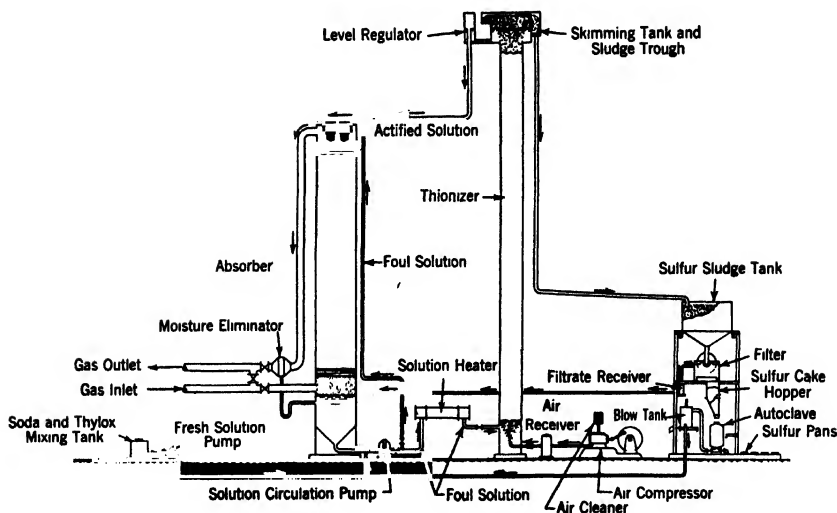
FIG. 5.   Flow diagram of the Koppers Thylox sulfur-recovery process.

dated Gas Company in Boston, Mass. At the right is a group of six thionizers arranged in a circle under a common sulfur-froth skimming tank at the top; at the left are the two gas scrubbers.

The installation of the Hudson Valley Fuel Company at Troy, N. Y., is shown in Fig. 7. The sulfur-slurry tank on the roof of the sulfur-handling building appears in the foreground with a stream of sulfur slurry flowing into it from the top of the thionizer. Behind the thionizer can be seen the top of the gas scrubber.

The completeness of hydrogen sulfide removal depends upon the design of the equipment and especially upon the amount of scrubbing surface in the gas scrubber. Actified Thylox solution has a definite but very tiny vapor pressure of hydrogen sulfide, which corresponds to around 0.2 to 0.3 grain of hydrogen sulfide per 100 cubic feet of gas. With adequate design, the process can reduce the hydrogen sulfide content of the gas so that the gas passes the empirical lead acetate paper test. Most plants have been designed, however, for 90 to 96 percent removal of the hydrogen sulfide. Several commercial plants have been built in America, Europe, and Japan to recover sulfur from gas by the Thylox process; they are listed in Table IV.

Sulfur is recovered from the sulfur-bearing froth overflowing from the top of the thionizer into the sulfur-slurry tank. Processing of the sulfur from this point depends upon how the sulfur is to be later used. Thylox sulfur may be marketed in several forms, such as a wet paste for agricultural sprays, a dry sulfur dust also for agricultural use and cast crude sulfur, and also as a redistilled purified sulfur suitable for any purpose requiring the pure element. In the United States, there is little incentive to produce a sulfur that competes with the inexpensive native Texas and Louisiana brimstone. The sulfur as originally recovered is a precipitated material of high chemical activity and of extremely
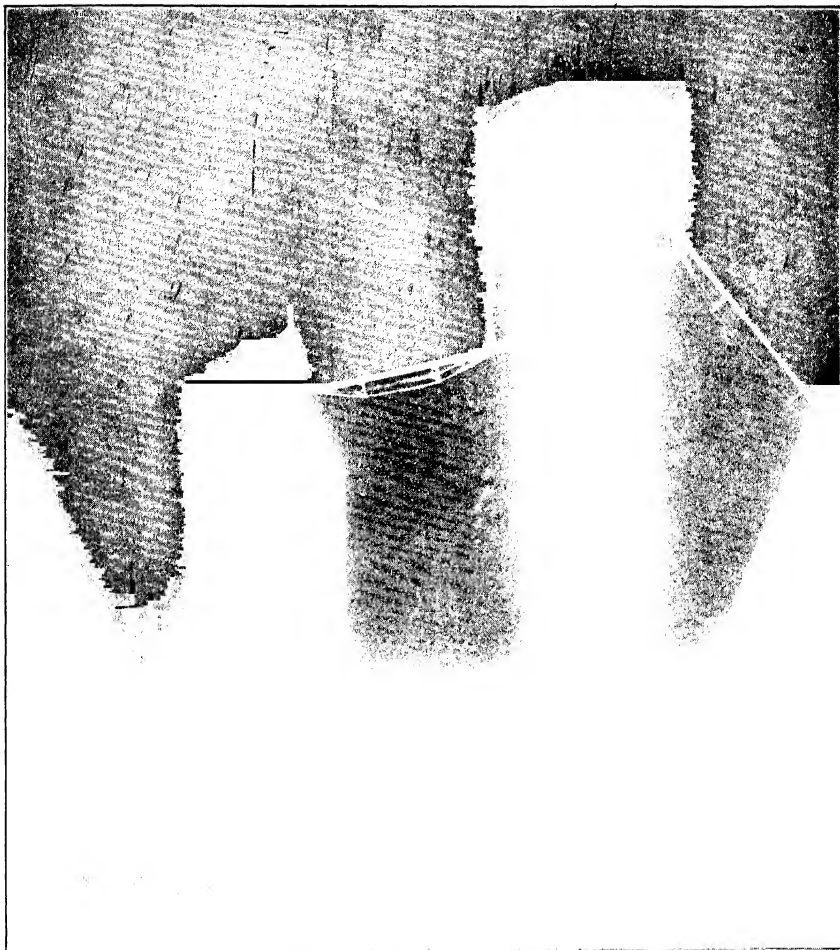
Fig. 6. View of Thylox sulfur-recovery process plant of the Boston (Mass.) Consolidated Gas Company.
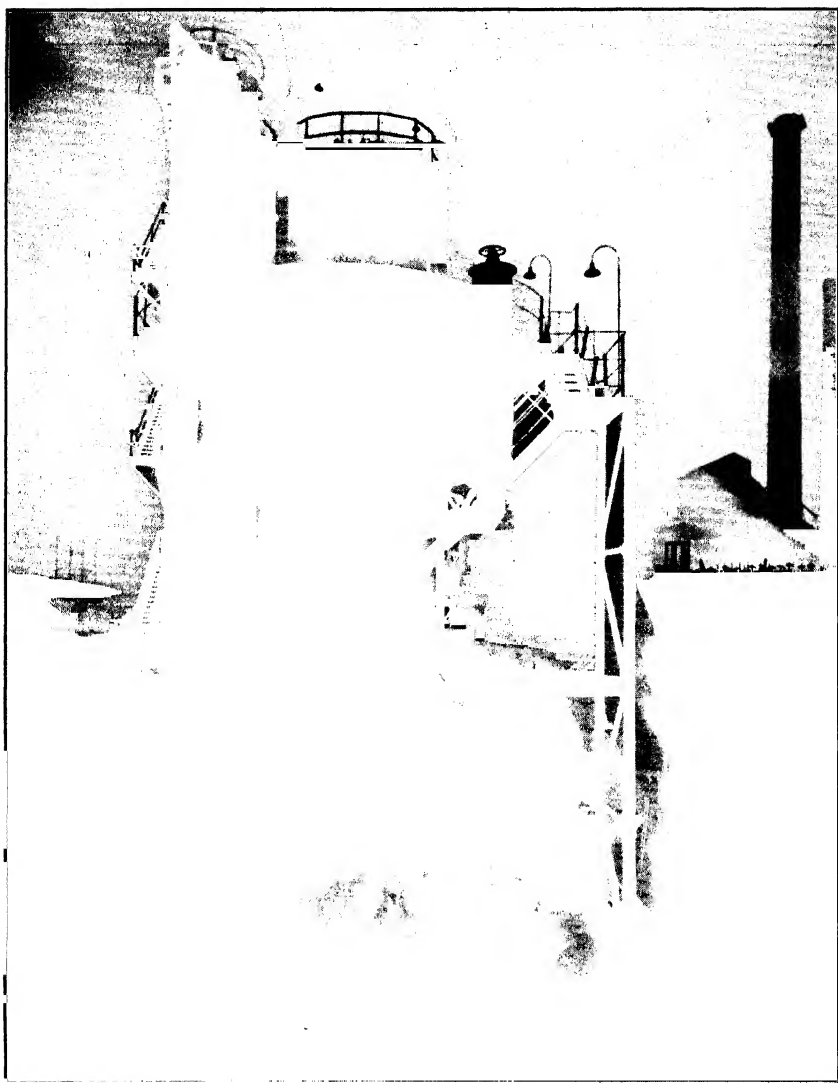
FIG. 7.   View of the Thylox plant of the Hudson Valley Fuel Company, Troy, N. Y.

TABLE IV

THYLOX GAS PURIFICATION PLANTS IN OPERA-
TION IN 1942 FOR SULFUR RECOVERY FROM
COAL GAS

Location	Capacity	
	Thousand Cubic Feet per Day	Pounds of Sulfur Removed from Gas per Day
United States		
Appleton, Wis.	1,300	600
Baltimore, Md.	18,000	9,000
Boston, Mass.	45,000	15,000
Racine, Wis.	10,000	3,500
Rochester, N. Y.	20,000	7,500
St. Louis, Mo.	12,000	5,700
Troy, N. Y.	16,000	8,000
Waukegan, Ill.	3,500	1,400
Total	125,800	50,700
Germany		
Gross Ilsede near Peine	9,400	8,400
Ewald Fortsetzung, near Rechlinghausen	8,500	4,700
Dortmund	14,000	10,600
Dortmund	17,500	13,200
Gelsenkirken-Schalke	28,000	12,500
Datteln	8,500	5,600
Datteln	6,800	4,600
König Ludwig near Rechlinghausen	17,500	9,000
Bonen, near Unna	9,500	4,800
Total	119,700	73,400
Japan		
Ube, Yamaguchi	13,000	6,500 (estimated)
Kyusyu, Yamaguchi	8,000	4,000
Total	21,000	10,500
Grand total	266,500	134,600

In addition to the above some installations
may be operating in Russia about which infor-
mation is unavailable. Also, there are a num-
ber of Thylox plants recovering sulfur from
gases other than coal gas, as follows:

	Thousand Cubic Feet of Water Gas per Day
United States	
Belle, W. Va.	75,000
Brooklyn, N. Y.	12,000
Seattle, Wash.	9,000
Japan	
Hikoshima, Yamaguchi	3,500
Toyokoatsu, Yamaguchi	17,500

small particle size, and applications that
take advantage of these properties have
been developed.[116] To study its use as an
agricultural spray, several extensive field
tests were made covering a period of sev-
eral years.[117, 118] As a result of this work,
it has been shown that sulfur produced by
this process is an exceptionally good ma-
terial for agricultural use as a fungicide,
and most of the Thylox sulfur produced in
the United States is now being devoted to
this purpose. In Europe, more emphasis
has been placed on the recovery of sulfur
itself to avoid the necessity of importation
of sulfur and sulfur ores. Consequently,
in the European plants, the sulfur is usu-
ally melted and distilled to recover a pure
product for general industrial use.

For the preparation of agricultural sul-
fur paste and dust, the sulfur slurry is first
filtered and washed free from salts. In
Fig. 8 is shown. the filter in operation at
the Troy, N. Y., plant. The wet sulfur
paste from the filters can be mixed with
other ingredients for spraying that may be
required and shipped as such to the user.
When it is desired to produce a sulfur dust,
the wet sulfur paste can be dried under
controlled conditions and converted to a

[116] Haynes, J. D., *Soil Sci.*, **25**, 443–6 (1928).
De Ong, E. R., *J. Econ. Entomol.*, **22**, 865–73
(1929).
[117] Sauchelli, V., *Ind. Eng. Chem.*, **25**, 863–7
(1933).
[118] Jacobson, D. L., *Chem. Markets*, **29**, 363
(1931).

FIG. 8.   Sulfur paste coming off continuous filter, Thylox process plant of Hudson Valley Fuel Company, Troy, N. Y.

dry powder. The product retains the advantages of the small particle size and the high chemical activity of precipitated sulfur produced in this manner. Figure 9 shows a view in the room containing the equipment for preparing sulfur dust and sulfur paste at the Boston plant.

If a sulfur for industrial applications is to be made, the Thylox sulfur is usually melted and cast into blocks.[118] This operation is ordinarily performed in an autoclave under pressure, because the melting point of sulfur is above the boiling point of water. When melted, the sulfur paste divides into two liquid layers, with the water on top and the heavier melted sulfur at the bottom. The melted sulfur is cast in cooling pans to produce a crude sulfur that can replace brimstone for uses not requiring too high purity in respect to arsenic and organic-matter contents.

In Europe, as above mentioned, the sulfur is usually distilled to make a pure product. The melted sulfur produced in the autoclave described in the preceding paragraph is charged to a fire-heated cast-iron retort connected to a condenser. At the beginning of the distillation, reactions occur between the sulfur and the organic impurities of the sulfur that form carbon disulfide and hydrogen sulfide. The first sulfur that distils consequently contains these compounds as impurities together with some organic matter that had not yet
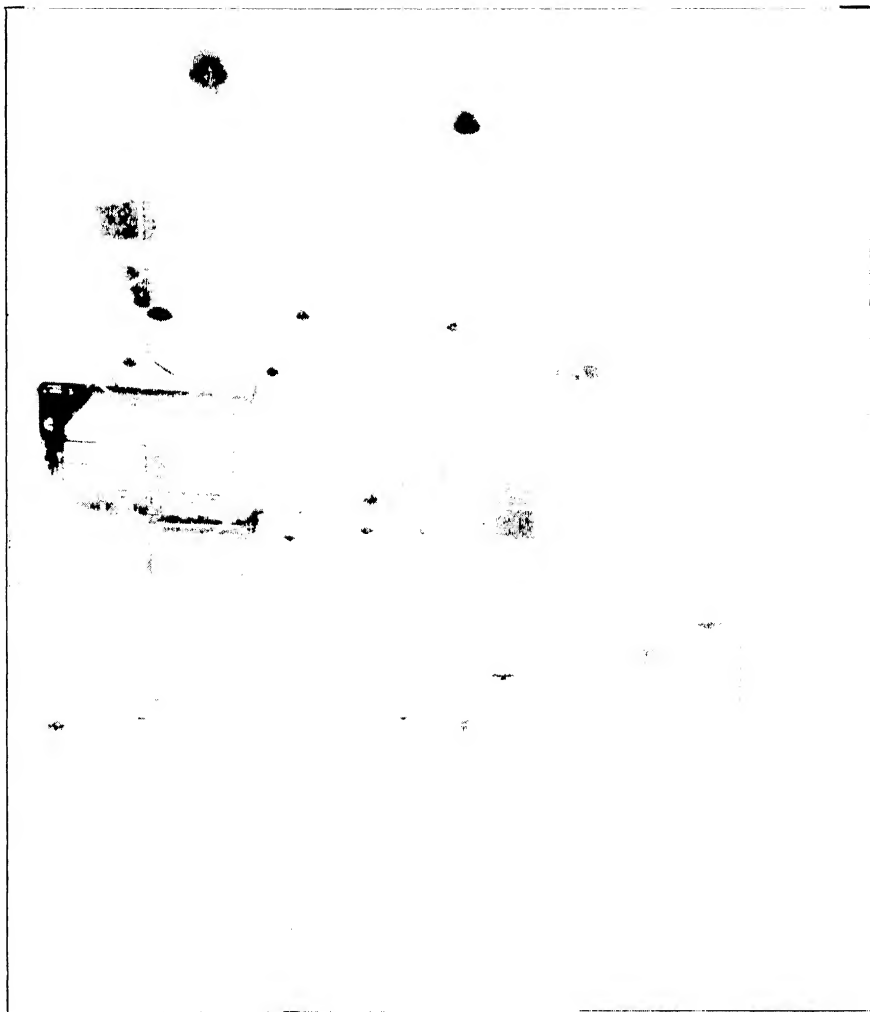
FIG. 9. Sulfur processing room of the Boston Consolidated Gas Company, Boston, Mass.

been completely destroyed by reacting with sulfur. However, these impurities distil off completely with a small amount of first runnings, after which most of the sulfur distils as a pure material. The first runnings containing the impurities are recharged to the retort with the next batch. The organic matter in the first runnings that had escaped being destroyed by reacting with the sulfur in the first distillation is ultimately destroyed in succeeding distillations. The products, hydrogen sulfide and carbon disulfide, eventually escape as uncondensed vapors from the condenser.

HYDROGEN SULFIDE REMOVAL BY ABSORPTION AND DESORPTION

If, when hydrogen sulfide is absorbed by a liquid, a proportion of the hydrogen sulfide exists in the liquid in the form of physically dissolved hydrogen sulfide, the solution has a hydrogen sulfide vapor pressure and is capable of transmitting hydrogen sulfide back to a gas. This principle was probably first applied in 1880 by Hill and Claus, who scrubbed hydrogen sulfide from gas by means of an ammonia liquor and heated the liquor to expel the hydrogen sulfide. Since that time much work has been done on the use of ammoniacal liquors to remove hydrogen sulfide, largely because the original simple process had many practical drawbacks that prevented commercial operations. For this reason, the processes involving mere absorption and desorption are discussed before ·the processes using ammonia.

In general, all absorption processes in which vapor pressures of the absorbed compound occur in the liquid require countercurrent gas scrubbers. Similarly, desorption or the sweeping out of the dissolved component with another vapor or gas also requires countercurrent equipment. Countercurrent gas scrubbers and desorbers are usually either bubble-plate columns or packed towers. The principles of such processes are explained in reference books on the subjects.[119] The theory is largely mathematical and physical, and a study of the reference books will reveal that there are definite relationships between liquor rate, gas rate, solubility of absorbed constituent, size of gas-contacting towers, and degree of absorption or desorption of the dissolved constituent. A typical application of absorption and desorption is found in the ordinary oil-washing process for recovering light oil from coal gas or for the recovery of gasoline from natural gas. The light-oil vapors are absorbed from the gas in a countercurrent scrubbing tower, and the absorbed vapors are stripped or desorbed from the wash oil by a current of steam usually in a bubble-plate column.

Liquids for absorbing hydrogen sulfide from gas need to have absorbing powers within certain practical limits. When the absorbing power is too low, the amount of liquid required per 1,000 cubic feet of gas is too high and pumping costs are excessive. The solubility of hydrogen sulfide in water, for example, is such that theoretically a water rate of 3,000 gallons and practically a water rate of about 4,000 gallons per 1,000 cubic feet would be required. This huge liquid volume is definitely impractical except under unusual conditions.

To enhance the solubility of hydrogen sulfide in water, solutions of mildly alkaline materials are used. The dissolved hydrogen sulfide undergoes partial dissociation in the liquid. The solubility of gases under such circumstances is explained by equilibrium diagrams of the following type: [120]

$$\underset{\text{Gaseous phase}}{H_2S} \quad : \quad \underset{\text{Liquid phase}}{H_2S \rightleftarrows H^+ + HS^-}$$
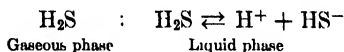
By the law of mass action, the equilibrium hydrogen sulfide concentration in the gaseous phase is proportional to the concentration of nonionized hydrogen sulfide in the liquid phase. In the liquid phase, ionization to form H^+ and HS^- ions occurs until

[119] Badger, W. L., and McCabe, W. L., *Elements of Chemical Engineering*, McGraw-Hill Book Co., New York, 2nd ed., 1936, 660 pp. Sherwood, T. K., *Absorption and Extraction*, McGraw-Hill Book Co., New York, 1937, 278 pp. Perry, J. H., et al., *Chemical Engineers' Handbook*, McGraw-Hill Book Co., New York, 2nd ed., 1941, 3029 pp.

[120] Taylor, H. S., *Treatise on Physical Chemistry*, D. Van Nostrand Co., New York, 1925, p. 848.

equilibrium between these ions and nonionized hydrogen sulfide is established. Consequently the concentration of nonionized hydrogen sulfide is but a fraction of the total hydrogen sulfide content of the solution, and the hydrogen sulfide solubility is greater than that of water. For example, if $\frac{1}{100}$ of the total hydrogen sulfide content of the solution is in the form of nonionized hydrogen sulfide, the solubility of hydrogen sulfide in the solution would be 100 times as great as the solubility of hydrogen sulfide in water.

The equilibrium between nonionized hydrogen sulfide and the ions HS^- and H^+ is expressed by the dissociation constant of hydrogen sulfide, K_{H_2S}. The dissociation constant is defined mathematically by the equation

$$K_{H_2S} = \frac{(H^+) \times (HS^-)}{(H_2S)}$$

in which (H^+), (HS^-), and (H_2S) are the concentrations in moles per liter of the ions H^+ and HS^-, and the nonionized hydrogen sulfide, respectively. This equation can be transposed thus:

$$\frac{(H_2S)}{(HS^-)} = \frac{(H^+)}{K_{H_2S}}$$

The first part of the last equation, $\frac{(H_2S)}{(HS^-)}$, is essentially the proportion of the total dissolved hydrogen sulfide that exists in the form of nonionized hydrogen sulfide, since (H_2S) is very small numerically compared to (HS^-). This proportion depends on the hydrogen-ion concentration as shown in the second half of the equation. Consequently, if the alkaline material dissolved in the water is such that the hydrogen-ion concentration is buffered at $\frac{1}{100}$ the value of the dissociation constant of hydrogen sulfide, $\frac{1}{100}$ of the total dissolved hydrogen sulfide will exist in the solution as nonionized hydrogen sulfide. The solubility of hy-

drogen sulfide in the solution will then be 100 times that in water, disregarding the comparatively slight effect of the ionic strength of the solution. For such a solution, a circulation rate of but 40 gallons per 1,000 cubic feet of gas would be necessary for hydrogen sulfide removal, which is a practical rate.

The dissociation constant of hydrogen sulfide is given in the literature as 0.91×10^{-7} at $25°$ C. An alkaline solution such as described above would need to be buffered at a hydrogen-ion concentration of $1/100 \times 0.91 \times 10^{-7}$, or 0.91×10^{-9}, or a pH of approximately 9.0. Hence, the selection of a suitable alkaline solution is merely the choice of a material that buffers the pH at a value not too far from 9.0.

In general, alkaline buffers are either (1) salts of strong bases and weak acids which may contain some excess of the weak acid, or (2) solutions of weak bases which may contain salts thereof with acids. With salts of strong bases and weak acids, buffer action is strongest when the hydrogen-ion concentration is about equal to the dissociation constant of the weak acid; and with weak bases the buffer action is strongest when the hydroxyl-ion concentration is about equal to the dissociation constant of the weak base. The hydroxyl-ion concentration of aqueous solutions is about 1×10^{-5} when the pH of the solution is 9.0. A desirable alkaline solution for hydrogen sulfide removal from gas would accordingly be one of the following two groups: (1) a salt of a strong base and a weak acid whose dissociation constant is not too far from 1×10^{-9}; or (2) a weak base whose dissociation constant is not too far from 1×10^{-5}.

Practically, alkali carbonates, borates, phosphates, and alkali salts of organic acids such as phenol, substituted phenol such as cresols, phenolsulfonates, chlorophenols and

nitrophenols, and amino acids are in the first category, which can be determined merely by measuring the dissociation constants or looking them up in the literature. Ammonia and almost all the stronger organic bases are in the second category. Reference books contain extensive lists of dissociation constants including many of the above.[121]

Seaboard Soda Liquid Purification Process. For the removal of hydrogen sulfide by absorption and desorption with alkaline solutions, soda ash is probably the cheapest alkaline material for the solution and air is the cheapest and most available gas for desorption. The process developed on this basis is known as the Seaboard soda liquid purification process. The first installation on a plant scale was in the year 1920, and the process and this installation have been thoroughly described by Sperr.[122] Because of its extreme simplicity and low operating cost, the process has found wide favor for removing hydrogen sulfide from various types of gases including coal gas, water gas, natural gas, and oil-refinery gas. More than fifty commercial installations have been built.

In this process, a solution of approximately 3.0 to 3.5 percent sodium carbonate is ordinarily used. The solution rate required depends somewhat upon the degree of purification required, the amounts of hydrogen sulfide and carbon dioxide in the gas, and the amount of air employed for actification or desorption. Within the range of conditions usually encountered in the purification of coal gases, the necessary solution rate is between 60 and 150 gallons per 1,000 cubic feet of gas. The air rate required for actification also depends on the

same conditions and is usually between 1.5 and 3 times the gas volume. The outlet air, which contains the hydrogen sulfide removed from the gas, may be objectionable because of its odor. For this reason, the air is led either into a tall stack so that it will become highly diluted before returning to ground level, or else to some units requiring air for combustion, such as steam boilers, gas producers, or coke-oven underfiring flues.[123]

The construction of equipment for this process can be extremely compact. Plants can be built having but one tall tower, with an air fan and solution pump. The tall tower is divided so that about one-half is used for the gas scrubber and one-half for the actifier and some space is left in the bottom for a pumping tank. A flow diagram of the Seaboard soda liquid purification process is shown in Fig. 10. Figure 11 shows an installation for this process for removing hydrogen sulfide from coal gas at the plant of Citizens Gas and Coke Company, Indianapolis, Ind. The tall tower with the stack along the upper half is the combined absorber-actifier tower containing the pumping tank in its base as shown in Fig. 10.

In addition to hydrogen sulfide, this solution removes hydrocyanic acid from the gas. In the actifier, or desorber, the hydrocyanic acid is largely converted to thiocyanate by the oxygen of the air and the hydrosulfides in the solution. Incidentally, the air oxidizes a small part, usually around 5 percent, of the hydrogen sulfide to thiosulfate. As both thiocyanate and thiosulfate formation consumes soda ash, it is necessary to add fresh soda ash to the system from time to time. Unless sufficient solution is lost mechanically or actually discarded, thiosulfates and thiocyanates will

121 Landolt-Börnstein, *Physikalisch-Chemische Tabellen,* Julius Springer, Berlin, 1923.
122 Sperr, F. W., Jr., *Proc. Am. Gas Assoc.,* 1921, 282–364.
123 Jacobson, D. L., *Gas Age-Record,* 63, 895–900 (1929).

accumulate to undesirable levels. Because the solution is made from the very cheap alkali soda ash, discard or loss of solution is an almost insignificant item of expense. These solutions have some value because of

FIG. 10. Flow diagram of the Seaboard soda liquid purification process.

their thiocyanate content and instead of being discarded they can be utilized by certain chemical manufacturers.

A possible modification of the Seaboard soda process is to combine it with final cooler operation at coke plants.[124] To do this, the regular final cooler serves also as a hydrogen sulfide absorber. Soda ash is

[124] Sperr, F. W., Jr., U. S. Pat. 1,961,255 (1934).

added to the liquor recirculation, and the fouled liquor is passed as usual through a cooling tower through which air is blown. Because the scrubbing surface is ordinarily limited in the design of final coolers, this method is not employed for a high degree of hydrogen sulfide removal. However, it serves as an extremely valuable emergency means for reducing the load on the regular purification system at times of excessive peak loads or when mechanical changes are being made.

Vacuum Carbonate Process. If the recovery of the desorbed hydrogen sulfide is desired, steam can serve as the actifying or desorbing gas.[125] The steam leaving the actifier can then be condensed and separated from the hydrogen sulfide gas. The solution can be actified under atmospheric pressure, 37 pounds of steam being required to produce about 1,000 cubic feet of vapor for desorption; or it can be actified under a partial vacuum as at 5 inches of mercury absolute, in which event only 7 pounds of steam is required to produce about 1,000 cubic feet of vapor. The vacuum carbonate process for hydrogen sulfide recovery utilizes the steam economy thus obtainable under a partial vacuum.

Figure 12 shows the flow diagram of this process. The general principles of the previously described Seaboard soda process and the vacuum carbonate process are similar, both being absorption-desorption processes. The differences between the two are (1) that steam at a reduced pressure is the desorbing vapor instead of air, and this steam is generated by boiling the liquid in the base of the actifier; (2) condensers are placed in the vapor lines leaving the actifier to condense the steam and separate it from the hydrogen sulfide; (3) a vacuum pump

[125] Sperr, F. W., Jr., and Hall, R. E., U. S. Pat. 1,533,773 (1925). Powell, A. R., U. S. Pat. 2,242,323 (1941).

FIG. 11.   Seaboard soda liquid purification plant of Citizens Gas and Coke Company, Indianapolis, Ind.

FIG 12   Flow diagram of the Koppers vacuum carbonate process

is operated to maintain the desired vacuum on the system and to deliver the recovered hydrogen sulfide to equipment for its utilization, (4) actification occurs at a higher temperature and coolers are ordinarily required on the actified solution; (5) since there is no oxygen in the actifier, the hydrocyanic acid remains unchanged and is recovered along with the hydrogen sulfide, and (6) oxidation to form thiosulfate and thiocyanate does not occur

Actification at higher temperatures introduces a new condition, which needs some theoretical discussion   However, actification under vacuum occurs at only slightly higher temperatures around 60° C, and the effect of temperature is not as significant as it is with processes not under vacuum that actify at about 100° C   Accordingly, the theoretical discussion of the effect of temperature will be deferred until the section in which processes using steam for actification are described

For the present it can be stated that there are essentially two effects of the slightly higher temperatures of vacuum actification   One is that a somewhat smaller volume of vapors for desorption is required, and the other is that slightly more carbon dioxide is expelled from the solution during actification   This second effect decreases the bicarbonate content of the solution until carbon dioxide desorption balances carbon dioxide absorption from the gas   The decreased bicarbonate content of the solution and the consequently higher normal carbonate content causes the hydrogen sulfide-absorbing power of the solution to increase

and permits operation with much lower solution pumping rates

Carbon dioxide absorption in practice is very slow compared with hydrogen sulfide absorption   Since gas scrubbers are normally designed for the more rapid hydrogen sulfide absorption, they have insufficient scrubbing surface to absorb much carbon dioxide   Thus, in the commercial application of the hot vacuum soda process for hydrogen sulfide recovery from coal gas, about one-seventh of a volume of carbon dioxide is removed from the gas per volume of hydrogen sulfide

As previously mentioned, the vacuum carbonate process recovers gaseous hydrocyanic acid from the coal gas along with the hydrogen sulfide   Cyanogen in this chemical form has a high value and may even have a greater value than the hydrogen sulfide   Consequently, the simultaneous recovery of cyanides is a major factor in connection with this process.

Figure 13 shows a commercial installation, in which 22 million cubic feet of coke-oven gas is treated per day at the plant of the Pittsburgh Coke and Iron Company.

Processes Using Steam for Actification
From previous discussion of the general theory of absorption and desorption processes for hydrogen sulfide removal, it is obvious that any alkaline solution buffered not too far from a pH of 9 0 can be used   In addition to soda ash, several solutions have been proposed, including potassium

Fig 13   View of vacuum carbonate process plant at the Pittsburgh Coke and Iron Company, Pittsburgh, Pa.

borate,[126] ethanolamines and diaminopropanol,[127] sodium phenolate[128] and salts of substituted phenols, potassium phosphate,[129] and the sodium salt of the amino acids.[130] The above solutions have been studied on a pilot-plant scale and some are in commercial use for other gases but not, as far as known, for hydrogen sulfide recovery from coal gas. Those employed commercially on other kinds of gas are discussed separately in the sections immediately following. In general, when gases contain hydrocyanic acid, as coal gas does, it is difficult to avoid entirely the formation and accumulation of compounds formed by the reaction of hydrocyanic acid with the solution. This necessitates either a preliminary removal of hydrocyanic acid from the gas or some treatment of the solution for the removal of the cyanogen compounds or regular discard of sufficient quantities of the solution. These considerations have discouraged the use of solutions containing more expensive materials.

Processes utilizing steam for actification at essentially atmospheric pressure operate at 100° C or above in the actifier. The effect of temperature on the operation of such processes is important. The absorption-desorption process in which the temperature in the absorption step approximately equals the temperature in the desorption step requires a desorption vapor volume about 1.5 to 3 times as great as the volume of the gas purified. When desorption occurs at around 100° C, the required volume of desorption vapors may be much less than that.

The volume of desorption vapors required at the higher temperature, say 100° C, is directly proportional to the effect of the increased temperature on the solubility of hydrogen sulfide. For example, if the solubility of hydrogen sulfide in the solution at 100° C is one-tenth as great as that at absorber temperature, the required volume of desorption vapors will likewise be one-tenth as great. This is evident from the accepted method of interpreting absorption and desorption tower performance by vapor-pressure graphs with an operating line.[131] If the hydrogen sulfide vapor pressure of the solution were ten times as great and the ordinates or vapor-pressure scale are changed to read ten times as great, the positions of the vapor-pressure line and the operating line would not change, and the number of theoretical plates required in the column would not change. Changing the vapor-pressure scale in this way indicates that the hydrogen sulfide content of the desorption gas is increased tenfold, or in other words that its volume has been reduced to one-tenth. The effect of the higher temperature of actification on the required volume of desorption vapor, steam, is thus the same as the effect on the solubility of hydrogen sulfide. The solution used for absorbing sulfide should be of such a type that its solubility for hydrogen sulfide is greatly reduced by higher temperatures.

The solubility of hydrogen sulfide in alkaline solutions as previously explained is a combined function of (1) solubility of hydrogen sulfide in water, or in water containing dissolved solids; (2) dissociation constant of hydrogen sulfide; and (3) the hydrogen-ion concentration in the solution. Since temperature affects all three, its effect on each will be discussed separately.

That hydrogen sulfide is less soluble in

126 Bragg, G. A., U. S. Pat. 1,920,626 (1933).
127 Bottoms, R. R., U. S. Pat. 1,783,901 (1930).
128 Shaw, J. A., U. S. Pat. 2,028,124 (1936).
129 Rosenstein, L., and Kramer, G. A., U. S. Pat. 1,945,163 (1934).
130 Bähr, H., and Mengdehl, H., U. S. Pat. 1,990,217 (1935).

131 See Perry, J. H., et al., p. 1166 of ref. 119.

hot water than in cold water, like almost all gases, is well known. Its solubility at 100° C is roughly one-third that at 25° C. For this reason, increased temperature tends to decrease the volume of desorption vapors required to about one-third.

The effect of temperature on the dissociation constant of hydrogen sulfide, K_{H_2S}, is of importance, since this constant changes materially with temperature. At higher temperatures, K_{H_2S} becomes greater, which means that H_2S is more acidic at higher temperatures. The exact value of K_{H_2S} at 100° C is not available, but extrapolation of data available at lower temperatures indicates that the dissociation constant is four times as great at 100° C as at 25° C. Consequently, the change in the dissociation constant of hydrogen sulfide at 100° C tends to increase the solubility of hydrogen sulfide about fourfold, and this effect is sufficient to somewhat more than offset the effect of temperature on solubilities in water. Thus the first two of the three factors mentioned are in opposite directions and are of about the same magnitude so that they essentially neutralize each other.

The effect of temperature on the hydrogen-ion concentration in the solution, which is the third factor listed above, is the remaining and the significant effect to be considered. With solutions of salts of weak acids with strong bases, the effect of temperature is to change the dissociation constant of the weak acid and to change the hydrogen-ion content in the same proportion. A desirable solution would be one with a weak acid whose dissociation constant increases most with increased temperature. With solutions of weak bases, the hydroxyl-ion content is proportional to the dissociation constant of the weak base and the hydrogen-ion content is equal to the dissociation constant of water divided by the hydroxyl-ion content, or

$$(H^+) = \frac{K_{H_2O}}{(OH^-)}$$

The effect of temperature on K_{H_2O} is rather great; at 100° C it is about fifty times as large as at 25° C. The effect of temperature on the dissociation constants of weak bases is usually rather small, so that the overall effect of higher temperatures is a large increase in the hydrogen-ion content of the solution.

The various processes employing steam for actification are essentially the same in principle and use the flow diagram shown in Fig. 14. The absorbent solution passes through the gas scrubber countercurrent to the gas and absorbs the hydrogen sulfide from the gas. The fouled solution passes through a heat exchanger and enters the top of a steam stripping column. At the bottom of this column is a boiling section, and the steam from the boiling solution passes up through the column and sweeps out or desorbs the hydrogen sulfide from the descending liquor. The steam and hydrogen sulfide mixture leaving the top of the stripping column pass through condensers to condense the steam from the recovered hydrogen sulfide. The hot solution leaving the boiling section passes through a heat exchanger and cooler and again enters the top of the gas scrubber.

These processes as previously mentioned have not been applied to the treatment of coal gases. However, those that are in commercial use for other gases are listed below and described briefly because they may be of future interest.

The Girbitol Process. Ethanolamines, and diaminopropanol and other amino compounds, have been used commercially for the recovery of hydrogen sulfide from natural gas and oil-refinery gases.[127, 132] Di-

[132] Bottoms, R. R., *Proc. Am. Gas Assoc.*, **1931**, 1071-82. Wood, W. R., and Storrs, B. D., *Refiner Natural Gasoline Mfr.*, **17**, 284-6 (1938).

ethanolamine, being a base of more desirable strength and requiring a lower solution rate, is ordinarily preferred to triethanolamine.

Amino compounds and organic bases, as above mentioned, include a great number of compounds. Several others have been

except that a two-stage process has been especially recommended to attain better steam economy. As strong solutions of phosphates are essential, the very soluble potassium phosphate is used. This phosphate process has been applied to gases free from carbon dioxide.
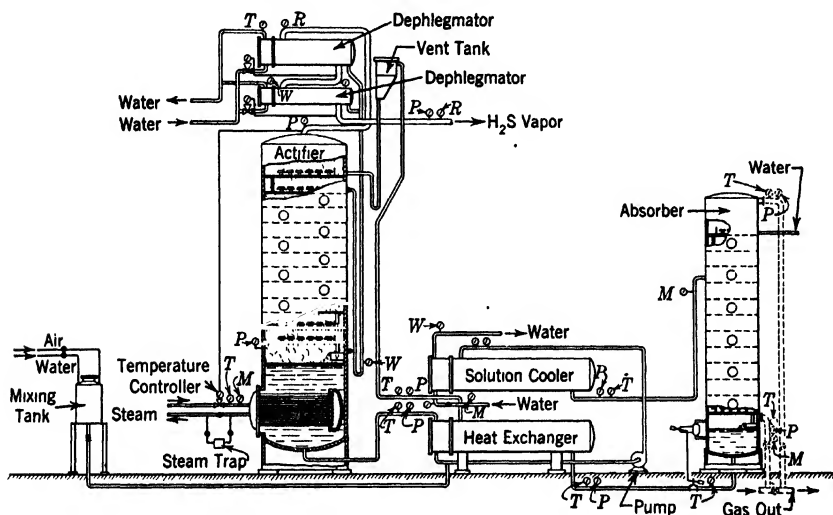
FIG. 14. Flow diagram of processes using steam for actification.

studied and suggested, among which may be mentioned dipiperidyd,[133] phenyl hydrazine,[134] a new diaminobutanol,[135] and miscellaneous organic bases.[136]

The Phosphate Process. Tripotassium phosphate, K_3PO_4, can be used for the recovery of hydrogen sulfide.[129, 137] The equipment is the same as that described,

The Phenolate Process. A process using a solution of sodium phenolate has been applied to refinery and natural gas.[128] Again, the equipment is the same as that for the previous processes. The operation of a commercial installation has been described by Carvlin.[138]

The Alkacid Process. In the so-called Alkacid process, the solutions used are sodium salts of amino acids, such as glycocoll and alanine.[130, 139] This process has been

133 Parkes, D. W., and Evans, R. B., U. S. Pat. 2,106,435 (1938).

134 Bottoms, R. R., U. S. Pat. 1,834,016 (1931).

135 Britton, E. C., U. S. Pat. 2,048,990 (1936).

136 I. G. Farbenindustrie G.m.b.H., U. S. Pat. 2,106,446 (1938) ; Brit. Pat. 470,440 (1937).

137 Rosebaugh, T. W., *Refiner Natural Gasoline Mfr.,* 17, 245–7 (1938). Zublin, E. W., U. S. Pat. 2,157,879 (1939).

138 Carvlin, G. M., *Refiner Natural Gasoline Mfr.,* 17, 225–38 (1938).

139 I. G. Farbenindustrie G.m.b.H., U. S. Pat. 2,011,386 (1935) ; Brit. Pat. 450,519 (1936). Bähr, H., *Refiner Natural Gasoline Mfr.,* 17, 237–44 (1938).

commercially applied at several plants at Leuna, Germany, in the synthetic ammonia and motor spirit industry to recover hydrogen sulfide from water gas.[140] Except for the composition of the solution used, this process does not differ from those described in the preceding paragraphs. When small amounts of oxygen are present in the gas, corrosive compounds can form in processes using organic nitrogen compounds. Methods to avoid corrosion have been made the subject of patents.[141]

Miscellaneous Proposed Processes. Several other liquids which have been proposed and have been experimented with on a laboratory scale cannot be classified definitely under the above group of processes. Among them may be mentioned magnesia suspensions,[142] lime with sodium chloride,[143] suspension of certain metallic sulfides in acidic solutions,[144] and solutions of alkaline materials in oils.[145] Magnesia and lime will function as weak bases because of their very low solubility in spite of the fact that they are strong bases. The formation of insoluble carbonates and the slowness of absorption of hydrogen sulfide have thus far prevented the commercial use of magnesia and lime suspensions, although fouled magnesia suspensions can be regenerated with exceptionally small quantities of steam.

SIMULTANEOUS RECOVERY OF SULFUR AND AMMONIA AND OTHER PROCESSES USING SULFUR DIOXIDE

An economical process for the simultaneous recovery of ammonia and hydrogen sulfide in the form of ammonium sulfate has been the goal of much research, including the pioneer work of Feld and Burkheiser.

Feld Processes. In Feld's work,[146] a process using zinc thiosulfate was first developed. This first process is essentially as follows. Gases containing ammonia and hydrogen sulfide are scrubbed with a zinc thiosulfate solution to precipitate zinc sulfide, and ammonium thiosulfate is formed and remains in solution. Sulfur, obtained later in the process, is burnt to generate sulfur dioxide, which is used to convert the zinc sulfide precipitate back to zinc thiosulfate solution. More gas is scrubbed with the zinc thiosulfate, etc., and the cycle is repeated continuously. Meanwhile, the concentration of ammonium thiosulfate increases. Portions of this solution are removed, treated with sulfur dioxide, and heated, which converts the ammonium thiosulfate to ammonium sulfate and sulfur. Most of the sulfur is burnt to provide the sulfur dioxide mentioned previously in this paragraph, and the ammonium sulfate solution is concentrated and crystallized.

Because of difficulties with the step in which zinc sulfide is treated with sulfur dioxide, the process did not operate properly, and further studies were made. Iron compounds were found to react better than the zinc compounds, but the method was still not as satisfactory as desired. Further studies led to the final process in which a solution containing ammonium thiosulfate and polythionates was used without requiring metallic compounds such as zinc or iron. This process, known also as the Feld thionate process, was operated successfully for a time at Konigsberg, Germany. The plant

140 Anon., *Coke and Smokeless Fuel,* **3**, 236–8 (1941).

141 I. G. Farbenindustrie G.m.b.H., Fr. Pat. 787,782 (1935). Bottoms, R. R., U. S. Pat. 2,031,632 (1936).

142 Sperr, F. W., Jr., U. S. Pat. 1,523,845 (1925).

143 Rue, H. P., *U. S. Bur. Mines, Repts. Investigations* **3178** (1932), 8 pp.

144 Ohme, H., Ger. Pat. 541,302 (1929).

145 Bähr, H., Wenzel, W., and Mengdehl, H., U. S. Pat. 2,161,663 (1939).

146 Feld, W., *Gas World,* **57**, 760 (1912) ; *Z. angew. Chem.,* **25**, 705–11 (1912). Raschig, F., *ibid.,* **33**, 260–2 (1920).

was shut down later, however, and has been replaced by other processes.

In the thionate process the gas is scrubbed with an ammoniacal liquor that removes hydrogen sulfide and forms ammonium thiosulfate in the solution. The ammonium thiosulfate is treated with sulfur dioxide to form various ammonium polythionates. These polythionates can absorb hydrogen sulfide and ammonia to form thiosulfate and sulfur, and this is the solution used for scrubbing hydrogen sulfide from the gas. As the cycle is repeated, the concentration of ammonium thiosulfate increases in the solution. As in the previous process, portions of the solution are withdrawn and treated with sulfur dioxide and heated to form sulfur and ammonium sulfate. Part or all of the sulfur is burnt to provide the sulfur dioxide required. The ammonium sulfate is concentrated and crystallized as in the first processes of Feld. The processes of Feld have received wide attention, and several critical reviews have been published describing them and various difficulties encountered, especially the step in which sulfur dioxide is used to convert thiosulfate to tetrathionate.[147]

Processes of Burkheiser. In the processes developed by Burkheiser,[148] sulfur recovered from hydrogen sulfide is burnt to form sulfur dioxide, which serves as an acidic material to remove ammonia from the gas to form ammonium sulfite. The process is also called the "sulfite-bisulfite" process, because the solution with which ammonia is scrubbed from the gas is actually an ammonium bisulfite solution, and absorption and reaction with ammonia form

the normal ammonium sulfite. This sulfite is converted back to bisulfite by sulfur dioxide. To obtain the sulfur required to produce the sulfur dioxide, the hydrogen sulfide is removed from the gas and is converted to sulfur in a preliminary and separate system.

The ammonium sulfite produced by the Burkheiser process is slowly oxidized by the air to form ammonium sulfate. It also loses ammonia to the air by vaporization and, therefore, has been less successful as a fertilizer than nonvolatile ammonium compounds.

Gluud's Combination Process. The process of Gluud to recover elemental sulfur by aeration of fouled ammoniacal iron suspensions has been described previously. Gluud has worked out a modification of this original method whereby ammonia and hydrogen sulfide are simultaneously recovered as either ammonium thiosulfate or sulfate.[149] A flow diagram of Gluud's process producing ammonium sulfate is shown in Fig. 15. The gas, previously washed to remove the hydrocyanic acid, passes through a gas scrubber where it is washed with an ammoniacal liquor to which some iron sulfate has been added. This solution absorbs ammonia and hydrogen sulfide from the gas, and the outlet solution is a complex mixture containing thio salts of ammonia. This solution goes through a saturator through which gases from a sulfur burner pass. Sulfur dioxide therein is absorbed, and the solution is pumped into a narrow aerating tower, 50 feet or more in height and full of solution. Compressed air is admitted at the bottom and in rising through the solution oxidizes the hydrosulfides and sulfites to ammonium thiosulfate. (In the original

147 Terres, E., and Overdick, F., *Gas- u. Wasserfach*, **71**, 49–53, 81–6, 106–10, 130–6 (1928). Overdick, F., *Z. angew. Chem.*, **43**, 1048–51 (1930).   Parker, A., *Gas Engr.*, **47**, 694–5 (1930).

148 Burkheiser, K., *Gas- u. Wasserfach*, **68**, 765–71 (1926). Terres, E., and Hahn, E., *ibid.*, **70**, 309–12, 339–43 (1927).

149 Gesellschaft für Kohlentechnik m.b.H., Brit. Pat. 362,669 (1930). Gluud, W., Klempt, W., and Brodkorb, F., *Ber. Ges. Kohlentech.*, **3**, 465–84 (1931).   Weittenhiller, H., *Glückauf*, **74**, 126–31 (1938).

Gluud process, it will be remembered, hydrosulfides are oxidized to elemental sulfur in a similar aerating tower. In the present tower, various polythionate and thio salts are present, with which the sulfur combines to form thiosulfate, so that little if any elemental sulfur is formed.)   The solution

previously mentioned. The solution of ammonium sulfate produced by the autoclave is concentrated in a vacuum evaporator and is crystallized to obtain ammonium sulfate. This process has been in operation on a pilot-plant scale at the Kaiserstuhl plant in Dortmund, Germany.
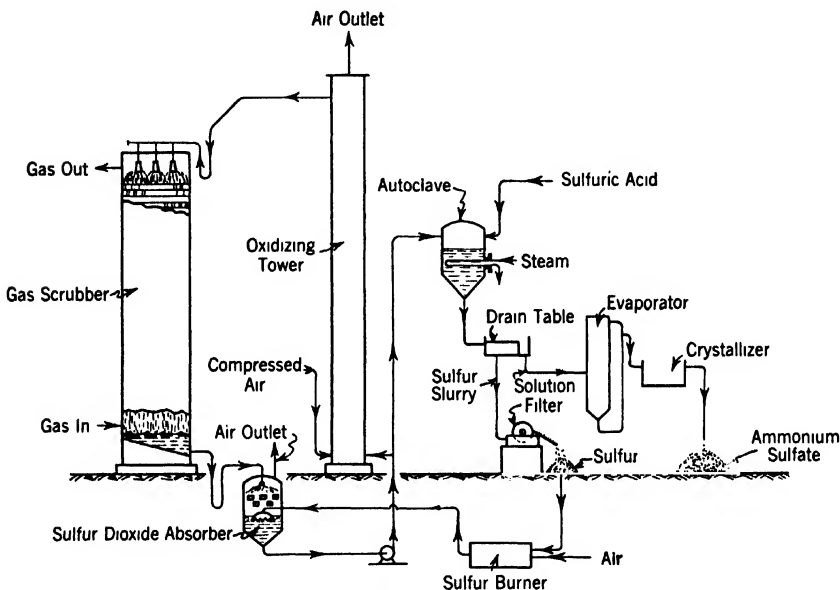
Fig. 15.   Flow diagram of Gluud's combination process for ammonium sulfate recovery.

leaving the aerating tower flows into the gas scrubber to absorb more ammonia and hydrogen sulfide in a continuous cyclic process. Ammonium thiosulfate accumulates in the solution, and quantities of the solution are withdrawn from time to time for conversion to ammonium sulfate. This is done by heating with sulfuric acid in an autoclave, in which the ammonium thiosulfate and sulfuric acid are converted to sulfur and ammonium sulfate. The sulfur is separated and part of it is burnt to form the sulfur dioxide required by the saturator

Koppers CAS Process. Another modification of the Feld and Burkheiser methods is known as the Koppers CAS process,[150] named for cyanogen, ammonia, and sulfur. In this process the hydrocyanic acid, ammonia, and hydrogen sulfide in the gas are all removed and recovered as sulfur and ammonium sulfate. Four gas scrubbers in series are used. In the first scrubber the gas is washed with a recirculated ammo-

150 Koppers, H., *Gas J.*, **188**, 643–4 (1929) ;
U. S. Pat. 1,971,964 (1934).   Hansen, C. J.,
U. S. Pat. 1,953,478 (1934), 2,029,262 (1936).
Eymann, C., U. S. Pat. 1,957,253 (1934).

niacal liquor containing sulfur. The hydrocyanic acid is thereby removed and ammonium thiocyanate accumulates in the solution. In the remaining three gas scrubbers in series, the gas is washed with an ammoniacal solution containing thiosulfates, sulfites, and polythionates. Sufficient concentrated ammonia liquor is also admitted at different points in the scrubbers so as to attain completeness of absorption of both ammonia and hydrogen sulfide. Some of the solution is withdrawn from the scrubbers, including also the first one which removes the hydrocyanic acid, and is treated as follows. It is divided into three parts: one part is regenerated by aeration to oxidize iron sulfides and ammonium hydrosulfide to sulfur; the second is treated with sulfur dioxide and filtered to recover sulfur; the third is decanted, treated with sulfur dioxide, mixed with filtrate from the sulfur dioxide treatment of the second part above, and heated under pressure at about 180° C. This treatment converts the thiocyanate and various thio salts to ammonium sulfate and sulfur, which are recovered. The process was operated on a plant scale for a time but because of corrosion difficulties it was later replaced by the Thylox process.

The Katasulf Process. The Katasulf process is probably the latest of the new methods for combined ammonia and hydrogen sulfide recovery to be placed in commercial operation.[151, 152] At Huls in the Ruhr section of Germany 25 million cubic feet of coke-oven gas per day was purified by this process. It is a combination process including both a high-temperature catalytic step and liquid washing steps at ordinary temperature, by which the hydrogen sulfide and the ammonia, together with the hydro-

cyanic acid and part of the organic sulfur, are all removed from the gas and recovered as ammonium sulfate. Studies made several years previously had resulted in the discovery that the hydrogen sulfide in coke-oven gas could be catalytically oxidized to sulfur dioxide. Catalysts mentioned include mixtures of activated carbon, silica gel, alumina and various metals,[153] and especially an activated carbon containing nickel.[151] Trouble due to deposition of carbon within the catalyst, a condition that has prevented commercial use of activated carbon for recovery of elemental sulfur from coal gases, does not occur at the higher temperatures required for the catalytic oxidation to sulfur dioxide.[154] Experimental work on a laboratory scale and later on pilot-plant scales resulted in the system that went into operation in the commercial plant.

Figure 16 shows the flow diagram of this process. The gas is first passed through a Cottrell tar precipitator, as it is important to prevent tar fog from being carried into the catalyst bed. The gas then enters a small preliminary scrubber in which a small part of the ammonia and hydrogen sulfide is removed by a part of the liquor recirculated through the main scrubber. Next, the gas passes through a humidifying tower in which it is warmed and saturated with water vapor at 40° C. It was claimed that the presence of this quantity of water vapor is necessary in order to completely convert hydrocyanic acid to ammonia when the gas later passes through the catalyst chamber.[155] The humidified gas then passes through gas-to-gas heat exchangers in which it is heated to about 400° C. Sufficient air to oxidize the hydrogen sulfide to ammonium sulfate and sulfur is added at this

151 Bähr, H., Brit. Pat. 310,063 (1927); U. S. Pats. 1,678,630 (1928), 1,889,942 (1932), 2,152,-454 (1939).
152 Bähr, H., *Chem. Fabrik,* 11, 10–20 (1938).

153 I. G. Farbenindustrie G.m.b.H., Brit. Pat. 310,063 (1927).
154 Dreyer, K., Brit. Pat. 473,248 (1937).
155 Bähr, H., Ger. Pat. 641,400 (1937).

point. The amount required depends upon the amount of hydrogen sulfide in the gas and the proportions that are recovered as sulfate and as sulfur respectively. At the commercial installation at Huls, Germany, the gas contained about 450 grains of hydrogen sulfide per 100 cubic feet, and the amount of air required was around 7 to 8 percent of the gas volume. This gas now

monium thio salts in solution. This recirculation passes through a heat exchanger to warm the water used in the previous step for humidifying the gas, and through a solution cooler, so that the main gas scrubber serves also as a gas cooler. A final washer scrubs the remaining sulfur dioxide and ammonia from the gas. A small stream of fresh water is kept recirculating over the
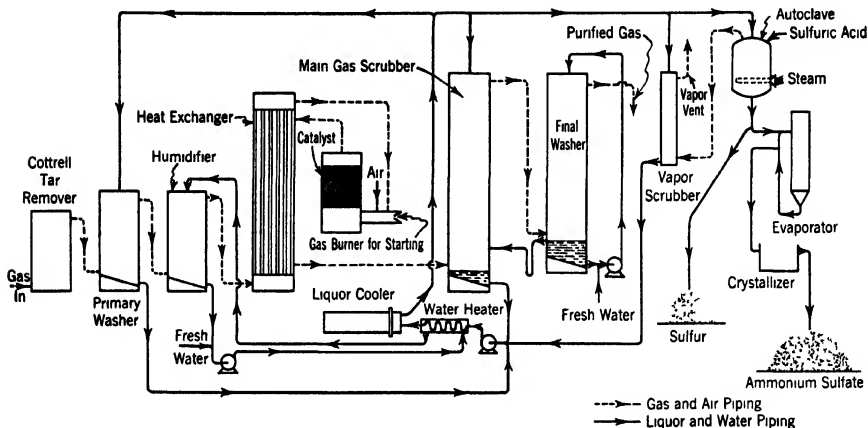
FIG. 16. Flow diagram of the Katasulf combination process for ammonium sulfate recovery.

passes through the catalyst bed and the hydrogen sulfide is catalytically oxidized to sulfur dioxide and the hydrocyanic acid is hydrolyzed to ammonia and carbon monoxide. The oxidation to sulfur dioxide, of course, evolves heat, and for this reason the gas temperature increases, the increase depending on the amount of hydrogen sulfide oxidized. The temperature rise is approximately 26° C for each 100 grains of hydrogen sulfide per 100 cubic feet, and at the plant treating 450-grain gas the temperature increase was about 120° C. This gas, after passing back through the above-mentioned heat exchanger to heat the incoming gas, enters the main gas scrubber where the ammonia and sulfur dioxide are removed by recirculation of liquor containing am-

final washer. The overflow from the final washer goes into the liquor in the main washer.

Ammonium sulfite and bisulfite would normally be formed from ammonia and sulfur dioxide. However, in this process, some hydrogen sulfide and ammonia are absorbed in the preliminary scrubber, forming ammonium sulfides, and this liquor is mixed with the liquor in the main scrubber. As a result little if any ammonium sulfite is formed. Instead, thiosulfates and polythionates are formed, and the main recirculating liquor is a mixture of such ammonium salts. The chemistry of the process has been discussed in Bähr's description.[152]

Either sulfuric acid or sulfur dioxide gas can be employed to convert these ammo-

nium salts to sulfate. To prevent the process from being too complicated, it was decided to choose sulfuric acid. The solution and sufficient sulfuric acid were added to an autoclave and heated. Some gases form in the autoclave and are scrubbed in another small scrubber to remove sulfur dioxide and ammonia that might otherwise escape. The autoclave treatment produces both sulfur and ammonium sulfate solution. The sulfur is separated, and the ammonium sulfate is concentrated and crystallized to produce the dry commercial salt.

The pilot plants in operation before erection of the commercial plant actually used sulfur dioxide from sulfur burners in the autoclave instead of sulfuric acid as described above. The procedure with sulfur dioxide, being more complex, was not used in the commercial plant.

Miscellaneous processes for combined hydrogen sulfide and ammonia recovery have been proposed, including variations in the original Feld and Burkheiser processes. For example, two or more gas scrubbers can be used in series for the Feld process, and ammonia gas or liquor can be added as required between the scrubbers, in order to improve the control over the absorption stage.[156] Also, the Feld and similar processes can be modified to produce an ammonium sulfate containing phosphates. These processes normally operate with solutions of ammonium thio salts, and this solution would be treated with phosphoric acid to produce the phosphate-containing final product.[157] Another method has been described in which zinc sulfate solution is employed to recover ammonium sulfate. Ammonia and hydrogen sulfide are both absorbed from the gas to form zinc sulfide and ammonium sulfate.[158] The zinc sulfide

is removed by filtration and roasted under controlled conditions to regenerate zinc sulfate for further use. The ammonium sulfate solution is concentrated and crystallized.

In the Burkheiser process, it will be recalled, ammonium sulfite is produced which partially oxidizes to ammonium sulfate in storage. In order to make this process more practical, it has been attempted to oxidize ammonium sulfite more efficiently. Even fifty years before the historic work of Burkheiser, Laming had proposed to convert ammonia to ammonium sulfate by adding sulfur dioxide and then oxidizing by treatment with air.[159] Burkheiser's work included improvements in a system using oxidation by air.[160] In the subsequent work of Vorländer and Lainau,[161] solutions of ammonium sulfite were oxidized to sulfate by aeration, using compounds of cobalt and vanadium as catalysts for oxidation.

Removal of Hydrogen Sulfide by Reactions with Sulfur Dioxide. In the preceding processes utilizing sulfur dioxide, the purpose was simultaneous recovery of ammonia and hydrogen sulfide as ammonium sulfate. Some methods have been proposed for hydrogen sulfide removal in which sulfur dioxide is used to convert the hydrogen sulfide to sulfur; an aqueous or an organic solution absorbs the hydrogen sulfide from the gas, and the foul solution is treated with sulfur dioxide. The free sulfur thereby formed is separated, and part of it is burnt to provide the sulfur dioxide required.

The complex nature of the reaction between hydrogen sulfide and sulfur dioxide has been mentioned before. The main difficulty to overcome is to obtain sufficiently

156 Hansen, C. J., U. S. Pat. 1,826,779 (1931).

157 Hansen, C. J., U. S. Pat. 1,944,978 (1934).

158 Cobb, J. W., *Gas J.*, 188, Inst. Gas Engrs. Suppl. 45 (1929).

159 Laming, R., Brit. Pat. 14,260 (1852).

160 Burkheiser, K., U. S. Pat. 1,034,974 (1912).

161 Vorländer, D., and Lainau, A., *J. prak. Chem.*, 123, 351–76 (1929); U. S. Pat. 1,925,739 (1933).

complete and rapid reactions for commercial application. The use of tar oils for such a process by Feld is well known. To hasten the reaction between hydrogen sulfide and sulfur dioxide, processes using thiocyanates in solution have been proposed.[162] Solutions containing organic bases have also been claimed to be useful.[163]

HYDROGEN SULFIDE REMOVAL BY ABSORPTION AND DISPOSAL OF SOLUTION

If only final traces of hydrogen sulfide need to be removed from gases, it may be practical to use an absorbing solution and to discard or otherwise dispose of the used solution. Such types of processes are not suitable for the removal of large amounts of hydrogen sulfide because purchase and disposal of large amounts of absorbing material would be required. Processes for the removal of traces of hydrogen sulfide have definite value. In preceding sections it has been mentioned that traces of hydrogen sulfide may be generated in otherwise clean gas by organic sulfur compounds or elemental sulfur.

Metallic compounds dissolved in oil, such as metallic soaps in gas oil, have been proposed as especially effective absorbents.[164] They have been recommended for removal of the minute amounts of hydrogen sulfide formed by bacterial action and other sulfur reactions in gas holders. In the operation of the Thylox process, the addition of small amounts of arsenic is normally required. Arsenic can combine with about half of its own weight of hydrogen sulfide; and, before the arsenic is added to the solution, it can be used to remove this amount of hydrogen sulfide from the purified gas.[165]

UTILIZATION OF RECOVERED HYDROGEN SULFIDE

The various processes that employ steam for actifying the solution used to absorb hydrogen sulfide from gas recover gaseous hydrogen sulfide. The recovered hydrogen sulfide can be utilized in different forms: (1) hydrogen sulfide as such, or the simple sulfides; (2) sulfuric acid; or (3) elemental sulfur.

The use of hydrogen sulfide as such is restricted by the fact that it must be compressed in steel cylinders for shipment. Some chemical processes can use alkaline solutions of hydrogen sulfides, such as calcium hydrosulfide and sodium hydrosulfide. These are very soluble materials and can be made by the absorption of hydrogen sulfide in milk of lime or caustic soda, respectively. After hydrogen sulfide and the simple sulfides become more available commercially, the chemical industry will doubtless find various uses for the material. Besides those in chemical manufacture, some study has been made regarding the possible application of hydrogen sulfide in agriculture as a fungicide in the treatment of seeds.[166]

Sulfuric acid, as previously mentioned, can be manufactured from hydrogen sulfide by processes similar to those using elemental sulfur. The hydrogen sulfide can be burnt, and the products of combustion with an excess of air present can be converted to sulfuric acid by known processes. The presence of ammonia or hydrocyanic acid in hydrogen sulfide will give rise to

162 Hansen, C. J., Brit. Pat. 394,917 (1933). C. Otto and Co. G.m.b.H., Ger. Pat. 610,840 (1935).
163 Girdler Corp., Brit. Pat. 419,479 (1934). C. Otto and Co. G.m.b.H., Brit. Pat. 430,865 (1935).
164 Hutchinson, W. K., and Dougill, G., Brit. Pat. 456,661 (1936).

165 Shoeld, M., U. S. Pat. 1,844,694 (1932).
166 Kiashko, P. E., *Rev. Applied Mycol.*, **15,** 669–70 (1935). Kvashnina, E. S., and Etmisheva, Z. S., *ibid.,* **16,** 26–7 (1936). Kapshuk, A. A., *ibid.,* **16,** 35 (1936).

nitrogen compounds in the sulfuric acid, and it is considered advisable to remove these ingredients. This is ordinarily done by washing the hydrogen sulfide gas with a small amount of water, since ammonia and hydrocyanic acid are easily removed by water washing.[167] When hydrogen sulfide is burnt, sulfur dioxide and water vapor are both formed.

$$H_2S + 1\tfrac{1}{2}O_2 = H_2O + SO_2$$
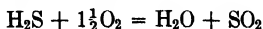
The presence of water vapor is undesirable in the products of combustion entering contact sulfuric acid plants. To avoid the difficulties caused by the presence of water vapor, the combustion gases can be cooled and dehydrated before passing through the converter.[168] Another way to avoid such difficulties is to use water-insensitive catalysts and to condense the sulfuric acid fractionally under controlled conditions in condensing equipment especially designed for the purpose.[169] A small commercial sulfuric acid plant making about 6 tons of sulfuric acid per day by this method has been described by Weittenhiller.[170] Cottrell electric precipitators will minimize the amount of sulfuric acid mist that tends to persist in the gases leaving the condensers when water vapor is present.

Elemental sulfur can be produced from hydrogen sulfide by partial combustion according to the equations:
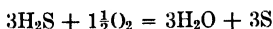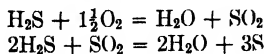
$$H_2S + 1\tfrac{1}{2}O_2 = H_2O + SO_2$$
$$2H_2S + SO_2 = 2H_2O + 3S$$

$$\overline{\rule{0pt}{0pt}\hphantom{3H_2S + 1\tfrac{1}{2}O_2 = 3H_2O + 3S}}$$

$$3H_2S + 1\tfrac{1}{2}O_2 = 3H_2O + 3S$$

The original Claus kiln for this purpose was developed around the year 1880. It used bauxite or iron oxide as a catalyst, and all the oxidation occurred in one large chamber. Its construction and operation have been described in reference books, especially by Lunge.[171] The original Claus kilns were rather large and cumbersome. The reaction gives off heat, and when the rates are increased there is a decided tendency for the catalyst to become overheated. The temperature in the kiln is controlled by balancing the feed of hydrogen sulfide plus air with radiation and other heat losses, a condition that restricts the working capacity within narrow limits. Improvements have been made in Claus kiln design mainly to improve the temperature control. One means of controlling temperature is to recirculate cooled vent gases. This method permits operation throughout a wide range of operating rates, but because of the high gas velocities through the catalyst bed the catalyst chamber must be large.

A more recent improvement is to burn part of the hydrogen sulfide separately and cool the vapors before they enter the Claus kiln.[172] By varying the proportion of hydrogen sulfide that is burnt separately and cooled, the quantity of heat evolved in the Claus kiln is changed and the temperature can be controlled. Of course, the total air and the total hydrogen sulfide entering the system must be kept in the proper proportion regardless of the proportion of hydrogen sulfide that is burnt separately. Since this method controls temperature without increasing the gas velocities in the kiln, the size of the kiln can be materially decreased. A commercial-size

[167] Schwarz, S. C., *Western Gas*, **3**, 113–8 (1927).

[168] Hechenbleikner, I., Oliver, T. C., and Spangler, S. F., U. S. Pat. 2,003,442 (1935).

[169] Von Girsewald, C., Siecke, W., and Wohlwill, M., U. S. Pat. 2,115,091 (1938). Koolman, C., Siecke, W., and Wohlwill, M., U. S. Pat. 2,172,617 (1939).

[170] Weittenhiller, H., *Glückauf*, **72**, 399–408 (1936).

[171] Lunge, G., *Sulfuric Acid and Alkali*, D. Van Nostrand & Co., New York, 1909, Vol. 2, p. 972.

[172] Bähr, H., and Mengdehl, H., U. S. Pat. 2,092,386 (1937).

Claus kiln modified in this manner has been built, and its operation has been described by Bähr.[173]

Much study has been given to the conversion of hydrogen sulfide and sulfur dioxide to sulfur at lower temperatures according to the equation

$$2H_2S + SO_2 = 2H_2O + 3S$$
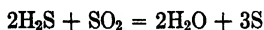
It has long been known that water catalyzes the reaction and also that the reaction is not so simple as the above equation would seem to indicate. Complex polythionic acids are also formed. Miscellaneous manners of operation with water as a catalyst and miscellaneous liquids instead of water have been proposed, none of which are known to be in commercial operation. Among them may be mentioned the classic use of tar oils by Feld,[174] thiocyanate solutions,[175] and organic bases.[176]

Modifications of Absorption-Desorption Processes. Two other types of processes in the absorption-desorption classification have not been included with the preceding methods because they are more complicated processes. One type makes use of carbon dioxide to help expel the hydrogen sulfide, and the other type combines hydrogen sulfide removal with ammonia recovery. Both have been studied at an earlier date than most of the processes thus far discussed.

The Petit process [177] employs a strong solution of potassium carbonate and regenerates the solution with air containing carbon dioxide. The regenerated solution, or part of it, may be boiled before it is again

used to scrub the gas. This process utilizes the stronger acidity of carbon dioxide to help desorb the hydrogen sulfide and thus a smaller volume of gases is needed for desorption.

Hultman and Pilo [178] used an ordinary soda ash solution for absorbing the hydrogen sulfide from the gas but combined several steps for desorption. The foul solution leaving the gas scrubber was first contacted with carbon dioxide to raise the hydrogen sulfide vapor pressure of the solution. Then the solution was actified under vacuum, hydrogen sulfide being recovered with some carbon dioxide. Part or all of the solution was then boiled to expel carbon dioxide, which completed the regeneration of the solution, and the solution was again used for scrubbing the gas. The carbon dioxide expelled by the boiling step was the source of the carbon dioxide used for contacting the foul solution before vacuum actification was applied.

Ammoniacal Solutions. The use of ammoniacal solution to absorb hydrogen sulfide from gas dates back to the original work of Hills [179] followed by the commercial developments of Claus.[180] They scrubbed the gas with ammoniacal liquor and employed heat to expel dissolved hydrogen sulfide and to regenerate the solution. After a trial on a commercial scale, the process was finally abandoned because of losses of ammonia.

The difficulties ordinarily encountered in removing hydrogen sulfide from gas by means of ammonia liquor may be attributed mainly to three causes: first, ammonia is an active absorbent for carbon dioxide which may be absorbed from the

173 Bähr, H., *Refiner Natural Gasoline Mfr.*, 17, 287–44 (1938).

174 Feld, W., Ger. Pat. 202,349 (1907).

175 Hansen, C. J., Brit. Pat. 394,917 (1933).

176 Girdler Corp., Brit. Pat. 419,479 (1934). C. Otto and Co., Brit. Pat. 430,865 (1935).

177 Petit, T. P. L., *J. Gas Lighting*, 131, 645–6 (1915).

178 Hultman, G. H., and Pilo, C. W., U. S. Pat. 2,094,070 (1937).

179 Hills, F. C., Brit. Pat. 1,369 (1868).

180 Bell, J. F., *Am. Gas Light J.*, 104, 39, 42–3 (1916).

gas instead of hydrogen sulfide, and there is usually a relatively large amount of carbon dioxide in the gas; second, ammonia liquors in equilibrium with the normal ammonia content of coal gas are rather weak, and a fairly large circulation rate is necessary for such liquor to absorb the hydrogen sulfide from the gas; and, third, it is difficult to attain sufficiently complete regeneration or elimination of the absorbed hydrogen sulfide without simultaneous loss of ammonia. Experience with processes for absorption of carbon dioxide and of hydrogen sulfide from gas has established the necessity of large scrubbing surfaces for carbon dioxide absorption. Consequently, if care is taken to keep the scrubbing surface down to the minimum required for hydrogen sulfide absorption, the troublesome carbon dioxide absorption can be kept at a minimum.[181] The necessary circulation rate can be reduced by recycling part of the ammonia production back to the hot gases in order to obtain a more concentrated ammonia liquor.[182] Also, by refrigerating the gases before scrubbing with ammonia liquor, the required circulation rate can be reduced.

In the years following the original work of Hills and Claus, the possible use of ammoniacal liquor was studied by many investigators who tried to overcome the disadvantages of the original processes. O'Neill[183] recirculated ammonia liquor through gas scrubbers and one or more plates above the ammonia still through which passed the ammonia and steam from the ammonia still. Lenze used refrigeration to cool the gas and then cleaned the

gas at especially low temperatures.[184] The main purpose of Lenze's process was removal of tar, naphthalene, and ammonia. Kemmer and Raschig[185] used the low-temperature treatment of gas of Lenze and the recirculation of ammonia mentioned by Davidson[182] to remove hydrogen sulfide from gas with ammoniacal liquor at low temperatures.

One of the problems mentioned above in ammonia processes is to obtain complete regeneration of fouled ammoniacal liquor without loss of ammonia. It is possible to use certain selective solvents to prevent loss of ammonia vapors with the hydrogen sulfide.[186]

When the value of ammonia is so low that recovery of ammonia is not profitable, an especially economical process for hydrogen sulfide removal is possible at coke plants heated with producer gas.[187] In this process, the ammonia is left in the gas, and the final cooler on the coke-oven gas and the producer-gas cooler are interconnected in the following manner. The liquor from the final cooler is pumped over the producer-gas cooler, and the liquid from the producer-gas cooler is pumped through cooling coils back to the final cooler. In the final cooler, the liquor absorbs about half of the ammonia and almost two-thirds of the hydrogen sulfide from the coke-oven gas. In the producer-gas cooler the ammonia and hydrogen sulfide are released into the producer gas. The hydrogen sulfide and ammonia remain in the producer gas and are burnt in the underfiring flues of the coke ovens. By

181 I. G. Farbenindustrie G.m.b.H., U. S. Pat. 2,083,213 (1931).
182 Davidson, W. B., Brit. Pat. 23,696 (1912) ; *J. Gas Lighting*, **122**, 948-54 (1913).
183 O'Neill, J. G., *Progressive Age*, **29**, 574-5, 707 (1911), **30**, 868-9 (1912).

184 Lenze, F., and Rettenmaier, A., *Gas- u. Wasserfach*, **69**, 689-91 (1926), **74**, 1169-72 (1931).
185 Kemmer, H., Brit. Pat. 370,243 (1932). Kemmer, H., and Raschig, M., Brit. Pat. 466,067 (1937).
186 Gollmar, H. A., U. S. Pat. 2,106,734 (1938).
187 Price, J. D., *Gas J.*, **204**, 142-3 (1933) ; U. S. Pat. 2,070,620 (1937).

this process, about 60 percent of the hydrogen sulfide is eliminated from the gas without operating additional units of equipment.

ORGANIC SULFUR COMPOUNDS AND THEIR REMOVAL

The organic sulfur compounds present in coal distillation gases include carbon disulfide, thiophene, carbon oxysulfide, mercaptans, and other compounds occurring in traces only, such as disulfides and thio ethers.

PROPERTIES OF THE ORGANIC SULFUR COMPOUNDS

Carbon disulfide, CS_2, is a volatile liquid at ordinary temperatures, soluble in oils and insoluble in water. Its main physical properties are as follows:

Boiling point	$46.3°$ C
Melting point	$-111.8°$ C
Solubility in water	0.2 gram per 100 grams water at $0°$ C
Density	1.2628 grams per milliliter at $20°$ C
Miscible with alcohol and hydrocarbon oils	

Carbon disulfide has an exceptionally low ignition temperature, and its mixtures with air are explosive throughout a much wider range of composition than most inflammable vapors. Chemically, carbon disulfide exhibits very feeble acidic characteristics. It reacts with alcoholic solutions of caustic alkalies to form xanthates, and with solutions of polysulfides to form thiocarbonates. Carbon disulfide is widely used in the chemical industry, and its value as an insecticide and a poison is important. The vapors of carbon disulfide are toxic, and, with processes in which their vapors can contaminate the air, attention should be given to this feature. Its toxicity

has been studied rather extensively,[188] and recommendations have been made that workmen should not be subjected to concentrations greater than 2 to 80 parts per million, depending on the length of exposure. Prolonged exposure to air containing 80 parts per million developed toxic effects, some of which were fatal to animals, and higher concentrations are of course more toxic.

Thiophene, C_4H_4S, is a liquid of about the same volatility as benzene, is insoluble in water, and is miscible with hydrocarbon oils. Its boiling point, $84°$ C, is so close to that of benzene that processes to remove benzene from gas will also remove thiophene with equal efficiency, and thiophene will contaminate the recovered benzene. When benzene recovery is practiced, the thiophene content of the debenzolized gas is usually insignificant and thiophene is then of importance only in connection with benzene refining. Chemically, thiophene is stable and inert. It is slightly more reactive than benzene, and will react only with strong chemical reagents.

Carbon oxysulfide, COS, also known as carbonyl sulfide, is a gas intermediate between carbon dioxide and carbon disulfide in its characteristics. It will dissolve slowly in strong aqueous solutions of caustic alkalies and is thereby decomposed to form a mixture of carbonate and sulfide. In alcoholic potash and soda it dissolves rapidly. Its solubility in water is 1.33 volumes per volume of water at $0°$ C, or about three-fourths that of carbon dioxide.

Mercaptans that occur in coal gas, such as methyl and ethyl mercaptans, are extremely volatile liquids. Methyl mercaptan boils at $7.6°$ C and ethyl mercaptan at

188 Wiley, F. H., and Hueper, W. C., and von Oettingen, W. F., *J. Ind. Hyg. Toxicol.*, **18**, 733–40 (1936). Brooks, A. L., *Ind. Med.*, **6**, 299–301 (1937). McNally, W. D., *ibid.*, **6**, 539–44 (1937), **7**, 295–303 (1938).

34.7° C. These liquids are insoluble in water and are miscible with hydrocarbon oils. Like carbon disulfide, they have weakly acidic properties and dissolve rapidly and completely in alcoholic potash. Aqueous solutions of caustic soda will absorb the mercaptans of lower molecular weight to form mercaptides. Mercaptans of higher molecular weight are less strongly held by aqueous caustic soda solutions. The mercaptans can be expelled from such solutions by boiling or by treatment with carbon dioxide. Mercaptans will also combine with many metallic compounds to form water-insoluble metallic mercaptides. Many of these metallic mercaptides are soluble in oils. Because of their characteristic penetrating odor, mercaptans are used widely to odorize domestic fuel gases in order to make leakage quickly noticeable.

The other compounds, as *thio ethers and disulfides*, are also oil-soluble volatile liquids. They occur in such minor concentrations that they are practically of no significance. These compounds, like thiophene, are largely removed by processes that recover benzene from the gas.

REMOVAL OF ORGANIC SULFUR COMPOUNDS

Unless it is necessary to reduce the sulfur content of gases to an unusually low level or unless coals of high sulfur contents are used, removal of organic sulfur compounds from gas has not been considered important. However, the desirability of gases of very low sulfur content for domestic use is becoming recognized, and of course certain chemical uses may require gases of exceptionally low sulfur content.

From the preceding paragraphs it will be noted that the different organic sulfur compounds vary in volatility from the fixed gas, carbon oxysulfide, boiling point −50° C, to thiophene, boiling point 84° C. How-

ever, carbon disulfide is the main compound in this group, accounting for about two-thirds of the total organic sulfur. As processes for the removal of organic sulfur must be effective for carbon disulfide, they are often termed carbon disulfide-removal processes. Of course, to attain very low total sulfur contents, they must also be effective for the removal of thiophene, carbon oxysulfide, and mercaptans.

Processes for the removal of organic sulfur may be classified in the following groups: (1) chemical absorption and disposal of spent absorbent; (2) absorption by solvents (oils) and desorption; (3) adsorption by solids (carbon) and desorption; (4) conversion to hydrogen sulfide or to sulfur dioxide at high temperature; and (5) refrigeration and condensation.

Chemical Absorption and Disposal of Spent Absorbent. Sulfided lime came into use at a very early date for removing carbon disulfide. Its use in England was almost universal until the year 1905, when the legal regulations that had restricted the permissible total sulfur content of domestic gas at about 20 grains per 100 cubic feet were revised. Since that time, sulfided lime purifiers have been discontinued by almost all gas companies. Sulfided lime contains calcium sulfides and polysulfides and probably absorbs carbon disulfide to form a calcium thiocarbonate compound, although the chemistry of the process has not been thoroughly studied. To operate this process, it is essential first to remove the carbon dioxide very thoroughly. The quantity of carbon dioxide makes the process difficult and expensive. It has also been proposed to remove carbon disulfide by means of other polysulfides. According to one process, carbon disulfide can be scrubbed from gas with an absorbent oil and the absorbed carbon disulfide can be removed from the oil by contacting with

sodium polysulfide solution [189]   Also, ammonium polysulfide can be used to scrub carbon disulfide from gas.[190]   The spent solution can be converted to thiocyanate by heating.   As far as known, none of these processes are employed commercially with the exception of lime sulfide purifiers remaining at a few small gasworks.

Absorption by Solvents and Desorption. In the foregoing discussion it was mentioned that carbon disulfide and thiophene are soluble in oil and are removed from gas by processes for benzene recovery.   In the ordinary wash-oil process, the gas is washed with an absorbent oil of low volatility, and the oil absorbs the benzene and other oil-soluble constituents from the gas.   The benzolized oil is then heated and steam-distilled to regenerate the absorbent oil for further use and to recover the benzene and other oil-soluble constituents.   The circulation rate of the absorbent oil is adjusted for efficient benzene and toluene recovery, which is the purpose of the process.   The wash-oil rate is inadequate for good carbon disulfide removal.   Such plants remove thiophene effectively, however, because an oil rate that will remove benzene from gas will also remove thiophene.   Benzolrecovery plants as ordinarily operated remove about half of the carbon disulfide from the gas.   A study of the removal of organic sulfur compounds during benzene recovery from gases made from high-sulfur Canadian coals has been reported by Dawson.[191]

To remove carbon disulfide from gas with absorbent oil, it is necessary to circulate a sufficient volume to absorb the carbon disulfide.   About 37 gallons is required per 1,000 cubic feet of gas at 20° C.[192]   **More** steam is needed in the light-oil **stripping** still when more absorbent oil is circulated because sufficient steam must be used per gallon of oil to strip out the benzene.   The amount of extra steam required is not so great when oil-to-oil heat exchangers are employed to preheat the benzolized oil, and these can be used without trouble when the light-oil plant is operating on purified gas. Further economy in steam consumption has been obtained by operating the stripping still under a partial vacuum or at an absolute pressure of 10 inches of mercury. The definite volume of sweep-steam required to strip the benzene from the absorbent oil can be obtained from only one-third the weight of steam that would have been necessary if the stripping column were operated at atmospheric pressure.

The design and operation of a plant for simultaneous benzol and organic sulfur removal from 7 million cubic feet of gas per day have been discussed by Cooper [192] and Hutchinson.[193]   The manner of operating such plants is also described in patents.[194] The gases before and after this modified light-oil plant were analyzed for different sulfur compounds.   The results indicated that 87 to 90 percent of the carbon disulfide and thiophene were removed, and 70 percent of the mercaptans, but none of the "volatile sulfur compounds," presumably carbon oxysulfide.   The removal of total organic sulfur was from 32 grains per 100 cubic foot inlet down to 8.6 grains outlet, or a removal of 73 percent.   Table V shows the analyses made of the inlet and outlet gases.

[189] Sell, G. E., and Klaiber, W. J., U. S. Pats. 1,785,365, 1,785,415 (1930).

[190] Hansen, C. J., and Eymann, C., U. S. Pat. 1,964,572 (1934).

[191] Dawson, K. L., *Eng. J.,* 11, 266–81 (1928).

[192] Cooper, C., *Gas World,* 108, Coking Sect., 27–31 (1938).

[193] Hutchinson, W. K., *Inst. Gas Engrs., Commun.* 175 (1937), pp. 8–44.

[194] Cooper, C., and Henshaw, D. M., Brit. Pat. 430,989 (1935).   Hutchinson, W. K., and Hopton, G. U., Brit. Pat. 443,089 (1936).

TABLE V

Removal of Organic Sulfur from Gas

Grains Sulfur per 100 Cubic Feet Present as	Gas Entering Plant			Gas Leaving Plant	Percent Removed
	Vertical Retorts	Inclined Retorts	Mixed Gas		
Mercaptans	2.2	1.1	1.8	0.5	70
Thiophene	5.0	8.3	6.1	0.8	87
Carbon disulfide	·19.6	16.9	18.7	1.9	90
Volatile sulfur compounds	5.6	4.9	5.4	5.4	0
Total	32.4	31.2	32.0	8.6	73

ADSORPTION BY SOLIDS AND DESORPTION

Activated carbon and silica gel can be used for light-oil recovery from gas; they also remove a major part of the organic sulfur. In Europe, a number of plants have been in operation using activated carbon for light-oil recovery. Hollings and Hay described such a plant treating 75 million cubic feet of coal gas per day at Beckton, England.[195] The use of activated carbon has also been discussed by Griffiths [196] and by Engelhardt.[197] To use activated carbon for light-oil removal, the gas must be free from hydrogen sulfide and heavy condensable hydrocarbons. It has been claimed that this process removes essentially all the carbon disulfide and thiophene from gas, or about 75 to 80 percent of the total organic sulfur.

CONVERSION OF ORGANIC SULFUR TO HYDROGEN SULFIDE OR TO SULFUR DIOXIDE AT HIGH TEMPERATURES

High-temperature processes for the elimination of organic sulfur compounds from gas have had a long history, dating back almost 100 years. According to a review of such processes by Carpenter,[198] a British patent was granted to Bowditch in 1860 for a process that comprises, first removing the hydrogen sulfide from the gas, reheating the gas to 140 to 215° C, passing it over iron oxide or lime to decompose the organic sulfur compounds to hydrogen sulfide, and then removing the hydrogen sulfide formed. A few years later, Harcourt proposed a process in which gas was passed through metallic iron turnings or wire at elevated temperature to decompose the sulfur compounds other than hydrogen sulfide. In 1875, Harcourt proposed passing the heated gas through a layer of small stones for the same purpose and also demonstrated his laboratory method for determining the total sulfur content of gas based on the same principle. Around 1878, Quaglio and Versmann, of Stockholm, proposed the use of clay balls impregnated with chlorides of different metals or the metals themselves. They proposed practically all the catalytic metals and specified 216 to 288° C as working temperatures.

Mechanical and chemical engineering problems prevented commercial application of such processes at these early dates, and the more recent developments of commercial processes have been the work of en-

195 Hollings, H., and Hay, S., *Chemistry & Industry*, **12**, 143–55 (1934) ; *Gas J.*, **205**, 741–4 (1934).

196 Griffiths, H., *J. Inst. Fuel*, **8**, 277–91 (1935).

197 Engelhardt, A., *Gas- u. Wasserfach*, **71**, 290–7 (1928), **77**, 189–93 (1934).

198 Carpenter, C., *Gas World*, **60**, 863–71 (1914).

gineers rather than of chemists. Pabst[199] applied the principles of blast-furnace stove operation for supplying heat to the gas, and a commercial plant treating about 4 million cubic feet of gas per day was built and operated at Portland, Ore., in 1908. In this system two checkerbrick-packed stoves were used. During the time the gas was being heated by passing through one of the stoves, the other stove was off the line and was being heated by producer gas. By passing the gas alternately through one stove and then through the other it was heated to about 650° C and was then passed through purifier boxes to remove the hydrogen sulfide formed. The process reduced the organic sulfur from 59 grains to 17 grains per 100 cubic feet, a reduction of about 71 percent.

In England, a process generally known as that of Carpenter and Evans was developed,[198] using fire-clay balls impregnated with a nickel salt and a reacting temperature of about 430° C. The design included gas-to-gas heat exchangers and tubes containing catalyst mounted in a setting where they were heated externally by combustion gases. The decomposition of carbon disulfide deposited carbon on the catalyst and formed hydrogen sulfide according to the equation:

$$CS_2 + 2H_2 = 2H_2S + C$$
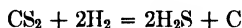
Accumulations of carbon were removed when necessary by purging with inert gas and carefully admitting air until further carbon dioxide was no longer formed. Two plants were constructed and placed in operation by the South Metropolitan Gas Company in London, one at the Old Kent Road in 1913, and one at the East Greenwich Plant in 1914, each of which handled about 10 million cubic feet of gas per day.

A reduction of 78 to 79 percent in organic sulfur, or from 35 to 40 grains per 100 cubic feet inlet to about 8 grains outlet, has been obtained in commercial operation.[198, 200] Subsequent operation has been changed somewhat by the use of a promoter with the nickel catalyst and operation at a lower temperature of around 300° C.[201] Under these conditions, it has been claimed that deposition of carbon on the catalyst is virtually eliminated without sacrificing the efficiency of organic sulfur removal stated above.[202]

. Continued study on the catalytic decomposition of organic sulfur compounds has resulted in many patents on mixtures of catalysts and promoters. The process of Fischer and Tropsch used a mixed catalyst containing copper and lead.[203] A process to convert carbon oxysulfide to hydrogen sulfide employed a copper sulfide catalyst containing copper and alkaline salts at 200 to 250° C.[204] Probably the most significant advance was the discovery that, in the presence of sufficient oxygen, catalysts could oxidize carbon disulfide to sulfur dioxide.[152, 205] The Katasulf process for hydrogen sulfide oxidation and recovery as ammonium sulfate was previously described under hydrogen sulfide removal; it oxidizes and removes some carbon disulfide. The operation of the Katasulf plant was primarily for hydrogen sulfide removal, but

199 Pabst, H. M., *Am. Gas Light J.*, 94, 407–9 (1911).

200 Evans, F. V., *J. Gas Lighting*, 128, 602–4 (1914), 129, 199–201 (1915).

201 Evans, E. V., and Stanier, H., *Proc. Roy. Soc.* (*London*), 105A, 626–41 (1924).

202 Hollings, H., and Evans, E. V., *Inst. Gas Engrs., Commun.* 146 (1936), pp. 7–8; *Gas World*, 105, 393–5, 411 (1936).

203 Fischer, F., and Tropsch, H., Brit. Pat. 254,288 (1925).

204 Società italiana ricerche industriali, Brit. Pat. 370,978 (1931).

205 Griffith, R. H., *Inst. Gas Engrs., Commun.* 175 (1937), pp. 44–64; *Gas World*, 107, 381–3 (1937). Griffith, R. H., and Plant, J., Brit. Pat. 489,398 (1938).

tests were made which showed a reduction in organic sulfur from 20 to 22 grains per 100 cubic feet inlet to 13 grains outlet.[152]

Other catalytic processes have been studied to remove the carbon disulfide as metallic sulfides. None of these processes are known to be applied to coal gas, and the reader is referred to the extensive bibliographies and the discussions by Huff and co-workers.[206, 207] Copper-uranium and cerium-uranium catalysts were reported to be effective for removing all the organic sulfur compounds, and copper-vanadium and copper-chromium were recommended for simultaneous absorption of hydrogen sulfide and organic sulfur;[207, 208] the catalyst can be regenerated by burning off the sulfur with air. Houdry[209] used a nickel oxide catalyst and also burnt off the sulfur from the spent catalyst. Another process[210] used an iron oxide-soda ash mixture at temperatures around 230° C.

Another process primarily for the conversion of carbon monoxide to nonpoisonous compounds incidentally converts most of the organic sulfur compounds to hydrogen sulfide. It employs an iron oxide catalyst at about 400° C to convert carbon monoxide to carbon dioxide and hydrogen by the well-known reaction

$$CO + H_2O = CO_2 + H_2$$
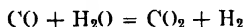
About 80 to 90 percent of the organic sulfur is converted to hydrogen sulfide.[211]

A process using an alkaline solution around 100° C to convert organic sulfur to hydrogen sulfide has been proposed.[212] Solutions suggested include amines such as triethenolamine and also alkaline salts of amino acids.

REFRIGERATION AND CONDENSATION

When coal gases are compressed and cooled to low temperatures to separate various fractions, the process can be so operated as to obtain a fraction containing the carbon disulfide. A condensate containing the carbon disulfide together with the hydrocyanic acid can be obtained by cooling the compressed gases to between −90 and −100° C by heat exchange with the gases leaving an expansion engine.[213]

PRESENT TRENDS

With the use of gas for greater numbers of new processes, there is a growing interest in more nearly complete removal of sulfur compounds. Also, gas-burning equipment is being made more automatic, and such equipment is expected to operate for long periods of time without attention. It is becoming more important to reduce corrosion from the gas and its products of combustion so as to minimize attention and maintenance. Some metallurgical uses of coal gas have already required gases of lower sulfur content. Greater attention to this subject is also being shown, and a growing number of applications that require gases of lower sulfur contents are to be expected. In the future it may become necessary to use poorer coals with higher sulfur contents. As such coals will produce gases of higher hydrogen sulfide and organic sulfur contents, the importance of sulfur-removal processes will increase still further.

[206] Huff, W. J., and Holtz, J. C., *Proc. Am. Gas Assoc.*, **1927**, 1436 9

[207] Huff, W. J., and Logan, L., *ibid.*, **1936**, 724–52.

[208] Huff, W. J., and Lusby, O. W., U. S. Pats. 1,900,882 (1933), 1,947,776 (1934).

[209] Houdry, E., *Natl. Petroleum News*, **30**, R 579 (1938).

[210] Roelen, O., and Feisst, W., U. S. Pat. 2,-110,240 (1938).

[211] Schuster, F., *Gas- u. Wasserfach*, **79**, 450–4 (1936). Müller, W. J., *Oesterr. Chem.-Ztg.*, **38**, 81–6 (1938).

[212] I. G. Farbenindustrie A.-G., Brit. Pat. 461,-001 (1937).

[213] Wucherer, J., *Gas- u. Wasserfach*, **78**, 118–21 (1935).

RECOVERY OF AMMONIA, CYANOGEN, PYRIDINE, AND OTHER NITROGENOUS COMPOUNDS FROM INDUSTRIAL GASES

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When coal or other solid, carbonaceous fuels are carbonized or gasified, there appear in the gas nitrogen, ammonia, cyanogen, and various nitrogenous heterocyclic compounds, such as pyridine and its homologs. They are, of course, primarily derived from the nitrogen contained in the fuel, though the nitrogen of the air which gets into the carbonizing and gasifying equipment through unavoidable leaks may contribute, by synthesis, to an insignificant degree.

The subject of nitrogen in solid fuels is dealt with in detail in Chapter 13, but the findings of various investigators will be briefly reviewed here. The proportion of nitrogen in American coals usually averages from 1 to 2 percent.[1] Lewes[2] gave the average as 1.4 percent, with the highest figure for coal as 1.8 percent and for peat as 3 percent. Knublauch[3] showed for German coking coals a range from 1.1 to 1.6 percent. Schilling[4] analyzed a variety of European coals and found German bituminous coals to contain from 1.1 to 1.5 percent, an English coal 1.45 percent, and Bohemian brown coals from 0.5 to 1.5 percent. Tichauer[5] gave the range as 1 to 2 percent, and he pointed out that younger coals usually contain more nitrogen than older ones. Drehschmidt,[6] who investigated a large number of European coals, found on an average for English coals 1.7, Westphalian 1.6, and Silesian 1.4 percent. McLeod[7] reported that the average nitrogen content of 80 coals was 1.43 percent. Caro[8] compared a German coal and its bony wash residue; the clean coal had 1.7 percent nitrogen, but the refuse analyzed from 0.9 to 1 percent, though according to its coal content of about 30 percent it should have analyzed only 0.5 percent nitrogen. This difference is due to the nitrogen content of the bony portion of the residue. Tidy[9] reported a Welsh coal with 0.9 percent, two English

[1] Fieldner, A. C., *U. S. Bur. Mines, Bull.* **22** (1913), Part 1, p. 30.

[2] Lewes, V. B., *The Carbonisation of Coal,* John Allan and Co., London, 1912, p. 247.

[3] Knublauch, O., *J. Gasbeleucht.,* **26,** 440–8 (1883).

[4] Schilling, E., dissertation, München, 1887, as quoted by Lunge, G., and Köhler, H., *Die Industrie des Steinkohlenteers und des Ammoniaks,* 5th ed., F. Vieweg & Sohn, Braunschweig, 1912, Vol. 2, p. 121.

[5] Tichauer, H., *J. Gasbeleucht,* **37,** 363 8, 381–5 (1894); *J. Soc. Chem. Ind.,* **14,** 143 (1895).

[6] Drehschmidt, H., *J. Gasbeleucht.,* **47,** 677–82 (1904).

[7] McLeod, J., *J. Soc. Chem. Ind.,* **26,** 135–9 (1907).

[8] Caro, N., Ger. Pat. 198,295 (1908). See also Vol. 2, p. 155, of ref. 4.

[9] Tidy, C. M., Private communication to Lunge, Lunge Köhler, ref. 4, Vol. 2, p. 121.

coals with 1.2 and 1.3 percent, and a Scotch coal with 1.4 percent nitrogen. Wolff,[10] in a broad survey of byproduct recovery, especially from producer gas, gave analyses of many coals; among them Ruhr coals averaged 1.6 and Saar coals 1.4 percent nitrogen. Terres [11] pointed out that no coal has been found as yet which does not contain nitrogen. Peat usually contains 0.9 to 2 percent, brown coal 0.6 to 2 percent, bituminous coal 1.2 to 1.6 percent, and anthracite 1 percent nitrogen. Trenkler,[12] in an economic study of power generation and the influence of recovered byproduct values on the cost of power, compared the nitrogen contents of various grades of coal; he found 1.6 percent for peat, 1.2 percent for brown coal, 2.4 percent for subbituminous, 1.4, 1.3, and 1.6 percent for various bituminous grades including culm, and 1.7 percent for a semi-anthracite.

In considering these various analyses it is well to remember that, as was pointed out by Gluud and Breuer [13] and by Gluud and Jacobson,[14] the Dumas and Kjeldahl methods of determining nitrogen in coal and coke are not distinguished by very great accuracy. However, since, according to Gluud, the older investigators usually reported too low results, 1.5 percent would appear to be a fair average for the nitrogen content of known and practically used coking coals in the more important industrial countries. ·

The question naturally arises how the nitrogen is bound in coal and what its origin is. Although a considerable amount of work has been done on this important subject, we are still very much in the dark about it, and it would seem that modern methods of investigation might do a useful job here. With a precise knowledge of the kind or kinds of nitrogen compounds contained in coal, a recovery more nearly complete, and perhaps in more valuable form, might become possible.

Since, according to Terres,[11] the wood of living trees such as beech, birch, and pines does not contain more than about 0.1 percent nitrogen, it cannot be the sole origin of coal nitrogen. For this reason various authors have expressed their belief that vegetable or animal proteins and their degradation products have become mixed with the decaying wood substance and are responsible for the seemingly abnormally high nitrogen content of coals. Anderson and Roberts [15] ascribed it to plant albumens and protoplasm. Rau and Hahn [16] found the leaves of ferns to contain 1.85 percent nitrogen, while fern humus contained 1.78 percent nitrogen. They concluded that there is no need for assumption of animal proteins as the original nitrogen-bearing substances, inasmuch as ferns and similar plants abounded in the flora of the carboniferous ages. Muhlert [17] also considered plant proteins to be primarily responsible but thought that infiltration of animal degradation products might have contributed. Terres,[11] however, favored animal protein as the mother substance of

10 Wolff, O., *Stahl u. Eisen,* **34**, 473–80, 579–83 (1914).

11 Terres, E., *J. Gasbeleucht.,* **59**, 519–21 (1916) ; *J. Soc. Chem. Ind.,* **36**, 586 (1917).

12 Trenkler, H. R., *Z. Ver. deut. Ing.,* **62**, 85–91 (1918) ; Gluud, W., and Jacobson, D. L., *International Handbook of the Byproduct Coke Industry,* The Chemical Catalog Co., New York, 1932, p. 115.

13 Gluud, W., and Breuer, P. K., *Ges. Abhandl. Kenntnis Kohle,* **3**, 227–37 (1918).

14 Gluud, W., and Jacobson, D. L., ref. 12, p. 108.

15 Anderson, W. C., and Roberts, J., *J. Soc. Chem. Ind.,* **18**, 1099–104 (1899).

16 Rau, O., *Stahl u. Eisen,* **30**, 1235–46, 1282–97 (1910).

17 Muhlert, F., *Die Industrie der Ammoniak-und Cyanverbindungen,* Spamer, Leipzig, 1915, p. 61.

coal nitrogen. Porter [18] sided with those favoring the plant proteins.

Attempts to isolate nitrogenous substances from coal—or at least to gain some idea of their constitution—by comparative pyrolysis of known organic nitrogen compounds have had only a fair amount of success. Pictet and Ramseyer [19] found that a distillate boiling at 110 to 265° C and 10 millimeters pressure, obtained from a benzol extract of coal, contained no nitrogen compounds. Pictet and Bouvier [20] distilled coal at 450° C and 15 to 17 millimeters pressure but found no ammonia in the aqueous distillate. However, the tar obtained gave on pyrolysis a considerable amount of ammonia and a high-temperature condensate containing bases of pyridine odor. Harger [21] thought that nitrogen occurred in coal in two or more essentially different compounds. He based his belief on the fact that during carbonization part of the coal nitrogen comes off as ammonia while another part stays behind in the coke. The former he considered to be in side chains and the latter in ring compounds. Harger quoted R. J. Friswell as having extracted coal with 50 percent nitric acid and having obtained "coal acids" which on heating with zinc dust gave ammonia, pyridine, cyanogen, and hydrogen cyanide. He also quoted Anderson as having made similar extracts with sulfuric acid and as having come to the conclusion that these extracts had a nitrogen ring nucleus. In another vacuum, low-temperature distillation of coal Pictet and Bouvier [22] found

bases in the tar obtained. Terres [11] pyrolyzed at 700 to 900° C a considerable number of organic nitrogen compounds containing different nitrogenous groups and linkages, to see if they yielded ammonia. Only those compounds which had an amino or substituted amino group gave ammonia. He concluded that coal must contain its nitrogen tied to carbon in a similar manner. In the same investigation, Terres extracted coal with a number of solvents. Whereas the coal contained 1.15 percent nitrogen the extracts (all from poor solvents) contained from 2.3 to 2.8 percent. The residue from a pyridine extraction still showed 1.06 percent nitrogen, so that not much enrichment could have been obtained in the extract (for which he gave no figure). This is particularly true in view of the great solvent power of pyridine with respect to coal. Cobb [23] also pyrolyzed known nitrogen compounds. Aminoacetic acid gave off ammonia over a wide range of temperatures. The nitrogen of the solid residue seemed to become more firmly bound as the temperature was increased. Shacklock and Drakeley [24] extracted solid fuels with 33.4 percent sulfuric acid and found that they could extract very substantial quantities of their nitrogen contents. The quantities extracted decreased in the following order: peat, lignite, subbituminous, bituminous, and anthracite; from peat 70 percent of the original nitrogen was extracted. They found monoamino acids to be present in all samples, amounting to 70 percent of the nitrogen extracted from the coals. Diamino acids were present in peat and lignite. Amides were present in all extracts and accounted for 15 to 20 percent of the extracted nitrogen.

18 Porter, H. C., *Coal Carbonization*, The Chemical Catalog Co., New York, 1924, p. 96.
19 Pictet, A., and Ramseyer, L., *Ber.*, **44**, 2468–97 (1911).
20 Pictet, A., and Bouvier, M., *Ber.*, **46**, 8342–53 (1913).
21 Harger, J., *J. Soc. Chem. Ind.*, **33**, 889–92 (1914).
22 Pictet, A., and Bouvier, M., *Ber.*, **48**, 926–33 (1915).

23 Cobb, J. W., *Fuel*, **124**, 167–74 (1922).
24 Shacklock, C. W., and Drakeley, T. J., *J. Soc. Chem. Ind.*, **46**, 478–81 (1927).

In normal coal carbonization, only part of the coal nitrogen is obtained as ammonia, the larger part remaining in the coke. This fact has been made the basis of the opinions of many of the investigators cited above, and it should therefore be pointed out that in coal hydrogenation practically all the coal nitrogen is released as ammonia.[25, 26] Since in coal hydrogenation the temperature rarely exceeds 450° C, and at this temperature in normal coal carbonization very little ammonia is given off, we may have in hydrogenation a splendid tool to add new and valuable information on the nature of nitrogen compounds in coal. A perusal of the existing literature in the field might unearth data from which this information could be deduced; or it might be obtained by running a series of tests on the hydrogenation of various nitrogen compounds to parallel the pyrolysis tests of Terres[11] and Cobb.[23]

NITROGENOUS PRODUCTS OF CARBONIZATION AND GASIFICATION

The most important nitrogenous product obtained in carbonization and gasification processes is ammonia. Next in importance is cyanogen or hydrogen cyanide, and finally, organic basic materials.

AMMONIA

Ammonia is not a heat-stable compound; at elevated temperatures it dissociates into its elements, nitrogen and hydrogen. Thus, Thau[27] noted measurable decomposition at 350° C, and Ramsay and Young[28] found decomposition to be pronounced at 500° C when the ammonia was in contact with porcelain or iron, but only at a much higher temperature when a glass tube was used. They found complete decomposition at 780° C in iron and 70 percent decomposition at 820° C in porcelain. Short[29] noted 28 percent destruction over firebrick at "full red heat." Haber[30] established the equilibrium conditions for ammonia at various temperatures in his famous investigation, which was to become the basis of the synthetic-ammonia industry. Bodenstein and Kranendieck[31] carried out fundamental researches concerning the decomposition of ammonia at elevated temperatures. Foxwell[32] assembled data on the thermal dissociation of ammonia with special reference to coke-oven conditions. Using ammonia in a stream of moist coal gas in coke-packed silica tubes, he determined velocity constants at temperatures from 520 to 850° C. The influence of surface materials, which had already been noted by Ramsay and Young,[28] was investigated more in detail by Foxwell,[32] who found that iron (particularly in its metallic form in coke-oven walls and in coke) was very detrimental, as was lime. Silica brick caused far less decomposition than an 80 percent siliceous brick. This great effect of the surface material had also previously been noted by White and Melville,[33] who found that fifty times as much

[25] Bergius, F., and Billwiller, J., Ger. Pat. Appl. B73,471 (1915); *Ges. Abhandl. Kenntnis Kohle,* **1,** 167–9 (1915–6). Fischer, F., *Conversion of Coal into Oils,* Ernest Benn, London, 1925, 297 pp.

[26] Fischer, F., and Tropsch, H., *Ges. Abhandl. Kenntnis Kohle,* **2,** 154–9 (1917).

[27] Thau, K., *Ann.,* **131,** 129–47 (1864).

[28] Ramsay, W., and Young, S., *J. Chem. Soc.,* **45,** 88–93 (1884).

[29] Short, A., *J. Soc. Chem. Ind.,* **26,** 581–5 (1907).

[30] Haber, F., and van Oordt, G., *Z. anorg. Chem.,* **43,** 111–5 (1905), **44,** 341–78 (1905); **47,** 42–55 (1905). Haber, F., and Le Rossignol, R., *Ber.,* **40,** 2144–54 (1907); *Z. Elektrochem.,* **14,** 513–8 (1908). Haber, F., Ger. Pat. 229,126 (1909); *Chem.-Ztg.,* **34,** 345–6 (1910).

[31] Bodenstein, M., and Kranendieck, F., *Nernst Festschrift,* W. Knapp, Halle, 1912, p. 99.

[32] Foxwell, G. E., *J. Soc. Chem. Ind.,* **61,** 114–25T (1922).

[33] White, A. H., and Melville, W., *J. Am. Chem. Soc.,* **27,** 873–86 (1905).

decomposition occurred on rough porcelain as on smooth glass; and by Woltereck,[34] who observed that dissociation started at 320° C in contact with metallic iron cloth, and at 420° C on oxide of iron. Heckel [35] had observed the deleterious action of iron in practical oven tests. When coal to which blast-furnace dust had been added was coked, the yield of ammonia "decreased tremendously." Mott and Mott and Hodsman,[36] like Foxwell, tried to imitate coke-oven conditions and did most of their work with coal gas containing from 1 to 2 percent ammonia. They observed in particular the effect of catalysts likely to be encountered in the coke oven and corroborated the testimony of previous investigators to the effect that iron and iron compounds (as encountered in old firebrick and in coke) are bad actors; but they found fused silica and carbon deposited from coal-gas decomposition to be contact materials of low activity. In fact, when fused silica was covered thickly with carbon, ammonia destruction at 900° C fell from 25 to about 13 percent. Hinshelwood and Burk [37] made a physicochemical study of the thermal decomposition of ammonia on various surfaces, such as silica, platinum, and tungsten. Tungsten is the most efficient catalyst. Schmidt [38] noted acceleration of ammonia decomposition in a porcelain tube and traced it to metallic iron produced from the tube by the reducing ac-

tion of the ammonia decomposition products.

But the thermal decomposition of ammonia is not the only cause of losses. Oxidation by air (from leaks in the ovens) may be a contributory cause. Thus Sommer [39] disclosed that at temperatures as low as 150° C oxidation is detectable, at 250° C it amounts to 5.86 percent, and at 450° C to 12.89 percent. Greenwood and Hodsman [40] and Greenwood [41] also dealt with the destructive effect of oxygen, using coal gas or nitrogen as the carrier for ammonia and oxygen, and working also with a mixture of air and ammonia. Destruction was greatest with air and least with coal gas. Mott and Hodsman [36] found ammonia mixed with air to be decomposed to the extent of 84 percent at 700° C, when passed over broken firebrick.

Fortunately protective agents and conditions allow preservation of ammonia to an extent far above the proportion its equilibrium would permit. Since hydrogen is the major decomposition product, it would be expected to suppress further destruction, at least to some extent. This is borne out by the findings of Mott and Hodsman,[36] who actually observed less decomposition in hydrogen and more in nitrogen than in coal gas. Coal gas, on account of its great hydrogen content, would be expected to take a place between hydrogen and nitrogen. Hinshelwood and Burk [37] also found hydrogen to retard ammonia decomposition but strangely did not note any effect of nitrogen. White and Melville [33] dissented, claiming that dilution with hydrogen or nitrogen is without influence "provided the time which each ammonia molecule stays in the tube is not changed."

[34] Woltereck, H. C., *Compt. rend.*, **147**, 460–1 (1908).

[35] Heckel, W., *Stahl u. Eisen*, **33**, 402–5 (1913); *Glückauf*, **49**, 361–4 (1913). Muhlert, F., p. 62 of ref. 17.

[36] Mott, R. A., *Gas World*, **78**, No. 2015, Coking Sect., 12–7 (1923); *Colliery Guardian*, **125**, 578–9 (1923). Mott, R. A., and Hodsman, H. J., *J. Soc. Chem. Ind.*, **42**, 4–12T (1923).

[37] Hinshelwood, C. N., and Burk, R. E., *J. Chem. Soc.*, **127**, 1105–17 (1925).

[38] Schmidt, A., *Z. angew. Chem.*, **38**, 1146–54 (1925).

[39] Sommer, F., *Stahl u. Eisen*, **39**, 261–6, 294–8, 349–53 (1919).

[40] Greenwood, H. D., and Hodsman, H. J., *J. Soc. Chem. Ind.*, **41**, 273–9T (1922).

[41] Greenwood, H. D., *Gas J.*, **161**, 750–1 (1923).

However, by far the greatest protective agent ever discovered is steam. Probably Thau [27] discovered it when he observed a reduction in decomposition to one-twentieth on switching from dry to moist gas. Mond [42] made practical use of this discovery when he proposed to gasify coal in the presence of excess steam to obtain larger ammonia yields. Drehschmidt [6] made the same observation, but White and Melville [38] dissented again and thought that the presence of water vapor somewhat increases decomposition. Woltereck [34] found the temperature of the initial decomposition lowered by steam. Simmersbach [43] favored the use of steam to increase ammonia formation, and Sommer [39] too, was convinced of the preserving action of steam, attributing it to the formation of ammonium hydroxide. Mott and Hodsman [36] made a fine contribution to the understanding of this problem. Using coke-oven gas containing from 1 to 2 percent ammonia, they obtained the data given in Table I. Pexton and Cobb [44] gasified coke at 900° C in an amount of steam similar to that used in a water-gas generator. Little ammonia survived dissociation. By trebling the amount of steam, however, they obtained total recovery of ammonia. Schmidt [38] tried to find the reason for this effect of steam and believed that it simply prevents the formation of metallic iron, which would serve as a decomposition catalyst.

Other, less practical agents have been observed and reported, chief among them hydrochloric acid. Though Mond [42] was apparently the first to disclose it, and even mentioned practical tests in which he

TABLE I

DECOMPOSITION OF AMMONIA AT 850° C IN COKE-OVEN GAS [16]

	Percent	Percent	Percent	Percent
Steam in gas	3.2	5.4	17.5	25.0
Decomposed ammonia	98.5	85.0	20.5	....

dropped brine or calcium chloride on the fuel bed of a Mond producer, it was left to Foxwell [32] some 30 years later to go into considerable experimental detail on this question. He believed the formation of ammonium chloride to be at the bottom of it. Schmidt,[38] on the other hand, thought that hydrogen chloride merely made the formation of metallic iron impossible and thereby eliminated the worst decomposition catalyst.

The other disclosures of protective agents are of even less importance. Thau [27] discovered that mercury vapors are half as effective as steam, and Sommer [39] found hydrogen sulfide to counteract the effect of oxygen on ammonia.

But purely mechanical means are also of great importance in preserving ammonia. Simmersbach [43] pointed out that a high velocity of the gases hinders the decomposition of ammonia. Cobb [45] observed that in a carbonizing test he obtained 22.5 percent of the coal nitrogen as ammonia at 800° C when the gases were removed at once from the hot part of the tube, but that the yield dropped to 17.2 percent when the gas passed through the red-hot part of the tube before its exit, and to 9.4 percent when it passed through red-hot coke. Sachs, as quoted by Terres,[11] was able largely to avoid decomposition of ammonia above 800° C by the use of a "hot-cold" tube. Greenwood [40, 41] agreed that the most important factor in ammonia preser-

[42] Mond, L., *J. Soc. Chem. Ind.*, **8**, 505–10 (1889). Lunge-Köhler, Vol. 2, p. 152, of ref. 4.

[43] Simmersbach, O., *Stahl u. Eisen,* **34**, 1153–9, 1204–13 (1914).

[44] Pexton, S., and Cobb, J. W., *Gas J.*, **163**, 160–73 (1923) ; *Gas World*, **78**, 619–30 (1923).

[45] Cobb, J. W., *J. Gas Lighting*, **126**, 329–31 (1914).

vation is its rapid removal from the hot retort.

A warning was sounded by Thau [46] in connection with the practical interpretation of many of the results reported above. He pointed out the danger of translating laboratory results into actual practice. Tests which he made on coke ovens showed that high temperatures of oven tops did not decompose ammonia. He explained this result by saying that, in normal oven operation, temperatures at which ammonia is decomposed at high rates are reached only when most of the ammonia has already been evolved; therefore, though the decomposition rate may be high, the effect on the total ammonia yield is negligible. Thau denied also the deleterious effect of iron compounds. He placed a layer of blast-furnace dust on the oven charge and found no reduction in ammonia yield. In view of the findings of other investigators, particularly of Heckel,[35] Thau perhaps may have failed to notice this effect only because he placed the iron-containing dust on the coal charge instead of mixing it with the coal.

CYANOGEN AND HYDROCYANIC ACID

Not only is ammonia lost by thermal dissociation into its elements; part of it is converted to other nitrogenous compounds, chiefly to hydrocyanic acid. The available literature does not often differentiate between cyanogen proper and hydrocyanic acid. The customary practice of using cyanogen as a collective term will be followed in the present chapter.

Various authors quite generally agree that under the conditions existing in carbonizing and gasifying equipment a considerable portion of the ammonia formed from the coal nitrogen is converted to cyanogen.

Thus it is not lost, but may eventually be recovered in a useful form either as such, in the form of cyanides, or even as ammonia, upon hydrolysis of the cyanogen. Considerable work has been done to clear up the mechanism of this conversion and to discover the best reaction conditions. About a hundred years ago, Langlois [47] passed ammonia over red-hot carbon and obtained ammonium cyanide. Bergmann [48] went into more detail and investigated the yields at various temperatures. Pure ammonia and charcoal gave 4 percent conversion at 800° C and 24 percent at 1,000° C. When the ammonia was diluted with illuminating gas, 60 percent was converted at about 1,150° C, 20 percent being unchanged and 20 percent decomposed. Iron was observed to be a decomposition catalyst, and the gas velocity was found to be of great importance. Temperatures above 1,100° C favored the reaction, probably because the speed of hydrogen cyanide formation then was much greater than the speed of ammonia dissociation. The illuminating gas used was held to be a diluent only, since carburation with propane did not change the yields.

White and Melville,[33] in their work on the thermal dissociation of ammonia, observed a 4 percent conversion to hydrogen cyanide (probably from the carbon dioxide which they used as a diluent). Carpenter,[49] experimenting with the reaction between ammonia and methane, found the critical temperature of formation to be about 800° C. At 855° C and a rapid rate of flow about 20 percent conversion was obtained. An extension of this work by Car-

46 Thau, A., *Brennstoff-Chem.*, 1, 52–8, 66–8 (1920).

47 Langlois, M., *Ann. chim. phys.*, (3), 1, 111–7 (1841).

48 Bergmann, E., *J. Gasbeleucht.*, 39, 117–22 (1896).

49 Carpenter, R. F., *Progressive Age*, 27, 575 (1909); *Chem. Abs.*, 3, 2747 (1909).

penter and Linder [50] established the stability of hydrogen cyanide in the presence of coal gas at 1,000° C and the fact that ethylene gives higher yields than methane. Poindexter [51] found that any carbonaceous material (illuminating gas, coke, benzene) will produce hydrogen cyanide from ammonia at 950 to 1,450° C and high velocities. At 1,200° C and contact times of 1 second, conversions as high as 70 percent were obtained, with only 5 percent of the ammonia lost by dissociation and 25 percent unchanged. Küster [52] imitated coke-oven conditions with respect to the concentrations of ammonia used, observing yields of hydrogen cyanide of 5.4 percent at 800° C, 12.8 percent at 900° C, 25.1 percent at 1,000° C, and 40.0 percent at 1,100° C. Bredig and associates [53] investigated this field very thoroughly, using acetylene, ethylene, methane, and carbon monoxide. They employed various catalysts, such as the oxides of aluminum, thorium, and cerium, and temperatures from 500° C to 1,100° C. Yields as high as 87.7 percent were reported. Küster [54] has given an excellent survey of the available literature and summarized the possibilities of hydrogen cyanide formation in the coke oven in the following equations:

(1)
$$C + NH_3 \rightarrow$$
$$HCN + H_2 \text{—} 39.5 \text{ kilocalories}$$

(2)
$$CH_4 + NH_3 \rightarrow$$
$$HCN + 3H_2 \text{—} 60.0 \text{ kilocalories}$$

(3)
$$C_2H_4 + 2NH_3 \rightarrow$$
$$2HCN + 4H_2 \text{—} 63.0 \text{ kilocalories}$$

(4)
$$C_2H_2 + 2NH_3 \rightarrow$$
$$2HCN + 3H_2 \text{—} 28.0 \text{ kilocalories}$$

(5)
$$CO + NH_3 \rightarrow$$
$$HCN + H_2O \text{—} 10.0 \text{ kilocalories}$$

In conclusion of his survey, Küster expressed the belief that reaction 4 is the probable one for coke ovens. This presupposes the existence of acetylene, which may well be formed from the methane of the gas. Inasmuch as acetylene is commonly suspected of being the mother substance of benzene and other aromatic hydrocarbons of coke-oven gas, such a supposition is quite reasonable, especially since its formation by thermolysis of methane and its homologs is well recognized.[55] The influence of water vapor on the reaction was disclosed by Wheeler.[56] The deleterious effect of carbon monoxide and oxygen was pointed out by Bergmann [48] and Breneman,[57] although their observations are in disagreement with the findings of other writers and should be checked. Some authors of well-known textbooks hold to the belief that cyanogen in coke ovens is largely formed from ammonia and incandescent coke,[58, 59] yet it may be concluded from the researches just presented that the reaction involving acetylene is at the bottom of it. In any event there is no question that cyanogen is a product of high temperatures and of secondary reactions. It is with certainty not derived from

[50] Carpenter, R. F., and Linder, S. E., *J. Gasbeleucht.*, **54**, 253 5 (1911).

[51] Poindexter, R. W., Jr., U. S. Pat. 1,584,137 (1926).

[52] Küster, H., dissertation, Braunschweig, 1928, 62 pp.; *Ges. Abhandl. Kenntnis Kohle*, **11**, 608 -19 (1931–3).

[53] Bredig, G., Elöd, E., and Demme, E., *Z. Elektrochem.*, **36**, 991–1003 (1930). Bredig, G., Elöd, E., and Müller, R., *ibid.*, **36**, 1003–7 (1930). Bredig, G., Elöd, E., and Kortüm, G., *ibid.*, **36**, 1007–23 (1930).

[54] Küster, H., *Brennstoff-Chem.*, **12**, 329–34 (1931).

[55] Pichler, H., dissertation, Vienna, 1929; Peters, K., and Meyer, K., *Ges. Abhandl. Kenntnis Kohle*, **9**, 625–40 (1928–9). Banc, M., Ger. Pats. 501,179 (1930), 594,124, 594,125 (1934); U. S. Pat. 1,773,611 (1930).

[56] Wheeler, T. S., U. S. Pat. 1,982,407 (1934).

[57] Breneman, A. A., *J. Am. Chem. Soc.*, **11**, 2–48 (1889).

[58] Gluud, W., and Jacobson, D. L., p. 119 of ref. 12.

[59] Lewes, V. B., p. 267 of ref. 2.

the coal substance itself by primary break-down, because it has never been observed in any low-temperature treatment of coal, be it extraction or distillation. However, it may be derived to a minor extent by pyrolysis from the nitrogenous compounds obtained as the primary products of coal decomposition, for Ruhemann [60] observed that pyridine on cracking yielded 6 to 7 percent by weight of hydrogen cyanide.

AROMATIC AND HETEROCYCLIC BASES

Under the term pyridine are commonly grouped a number of aromatic and heterocyclic bases, such as aniline, pyridine, picolines, lutidines, collidines, and quinolines. Since their most important representative is pyridine, and since this is standard practice, the term will be used collectively hereafter.

It has been pointed out in previous pages that the nitrogen compounds contained in coal may be partly of cyclic structure. Maillard [61] made a very interesting test to imitate nature and synthesize coallike materials which would give pyridine on carbonization. He was able to condense sugars with various amino acids, and he found that the resulting humuslike substances readily yielded cyclic nitrogen compounds on heating. On this he based his belief that the carbohydrates derived from cellulose combined with amino acids formed by hydrolysis of prehistoric protein material to form compounds, now existing in coal, which give rise to the formation of pyridine during the coking operation. Since the union of amino acids and sugars is observable at temperatures as low as 37° C, the proper conditions certainly existed during coal formation. Thus the appearance of cyclic and hetero-

cyclic bases in the products of coal carbonization is not surprising. They have been observed even in low-temperature carbonization, in coal extractions, and in coal hydrogenation. Only small quantities of the bases, however, were in the form of pyridine and its near homologs (so well known from coke-oven practice); the greater part was in the form of the higher homologs. Börnstein [62] distilled coals ranging from high-volatile to low-volatile grade at 450° C and found bases other than ammonia in the tar. Terres [11] found increased nitrogen contents in extracts obtained with various solvents. Pictet and Bouvier [20] noted pyridine on pyrolysis of a vacuum tar made at 450° C. In a later paper,[22] the same authors found the vacuum tar itself to contain bases, though less than 5 percent. Harger [21] quoted Friswell as having obtained pyridine on heating "coal acids" obtained by treatment of coal with 50 percent nitric acid. Jones and Wheeler [63] vacuum-distilled coal and mentioned that the vacuum tar contained small quantities of pyridine. Schneider [64] distilled brown coal with steam; he found no bases up to 450° C, but they appeared when the coal was heated above that temperature. Fischer and Tropsch [26] obtained amines such as pyridine on treatment of coal with hydrogen iodide and phosphorus. Wellington and Cooper,[65] in their book on low-temperature carbonization of coal, reported that small quantities of pyridine, picolines, and lutidines were observed in various tar fractions. Finally, the synthesis of pyridine and its homologs during carbonization of

[60] Ruhemann, S., *Erdöl u. Teer,* **5,** 455–8 (1929).

[61] Maillard, L. C., *Compt. rend.,* **157,** 850–2 (1913).

[62] Börnstein, E., *J. Gasbeleucht.,* **49,** 627–30, 667–71 (1906).

[63] Jones, D.. T., and Wheeler, R. V., *J. Chem. Soc.,* **105,** 140–51T (1914).

[64] Schneider, W., *Ges. Abhandl. Kenntnis Kohle,* **2,** 80–127 (1917).

[65] Wellington, S. N., and Cooper, W. R., *Low Temperature Carbonisation,* Charles Griffin and Co., London, 1924, p. 127.

coal may contribute to the final yield observed in gas and tar. Tschitschibabin and Moschkin [66] discovered that pyridine bases could be synthesized conveniently from ammonia and acetylene at temperatures around 400° C. Since the formation of acetylene from methane by thermolysis is known,[55] the conditions for such a synthesis should exist in a coke oven or other gas-making equipment. Such a synthesis, first suggested by Berger,[67] would seem particularly plausible since Burgess and Wheeler [68] found in the gases of their vacuum distillations of coal appreciable quantities of acetylene—0.5 percent at 300° C. The Tschitschibabin reaction starts at 300° C and is in full swing at 400° C, so that the proper reaction conditions are present.

YIELDS OF NITROGENOUS BASES ATTAINABLE

The discussion so far has dealt with the more theoretical aspects of the origin of nitrogenous compounds in fuel gases and the factors influencing their production and their stability at production temperatures; the actual conversion of coal nitrogen into useful products and the practical means by which it can be influenced will now be examined. Since many writers have covered the field broadly it will not always be possible to differentiate between ammonia, cyanogen, and pyridine, and the three will therefore frequently be lumped together. Where separation is possible they will be handled in the usual sequence.

Nitrogen compounds from coal are normally thought of in connection with coke ovens and gas-house retorts. However, they are quite generally produced wherever solid fuels of any kind are carbonized or gasified,

as in producers, water-gas machines, and blast furnaces. Naturally, conditions are not always favorable for their preservation, but the main factor is the tremendous dilution in all equipment but the coke oven and gas retort. This dilution, although it is in itself favorable to increased ammonia production, makes the recovery of the nitrogen compounds generally uneconomical. This was pointed out by Anderson and Roberts,[15] who emphasized that 130,000 cubic feet of blast-furnace gas must be handled per ton of coal compared with 11,000 cubic feet in coke-oven practice.

In the carbonization of coal at low temperatures (less than 500° C) the yields of ammonia and pyridine are very small, and cyanogen is totally absent. In fact, whenever yields approaching those of the coke oven are reported, they can usually be taken as an indication that the products of carbonization were overheated somewhere in the apparatus. Börnstein,[62] distilling high- and low-volatile coals at 450° C, found ammonia and pyridine, but no cyanogen. Bauer [69] carbonized a medium-volatile coal at 400° C and noted very low ammonia yields. Parr and Olin [70] reported 0.8 pound of ammonia per ton of coal. Pictet and Ramseyer [19] distilled coal at 450° C but did not even mention nitrogen compounds in their products. Pictet and Bouvier,[20] in another report on a vacuum distillation at 450° C, expressly stated that no ammonia or ammonium salts were obtained, but that the vacuum tar on pyrolyzing at red heat yielded abundant ammonia and traces of pyridine. In another vacuum tar the same investigators found bases, but no ammonia. Jones and Wheeler [63] found mere traces of ammonia and pyridine in

[66] Tschitschibabin, A. E., and Moschkin, P. A., *J. prakt. Chem.*, (2), **107**, 109-21 (1924).

[67] Berger, C., *Rev. gén. chim.*, **13**, 246-8 (1910).

[68] Burgess. M. J., and Wheeler, R. V., *J. Chem. Soc.*, **105**, 131-40 (1914).

[69] Bauer, A., dissertation, Rostock, 1908. See Gröppel, H., *Ges. Abhandl. Kenntnis Kohle*, **1**, 96 (1915-6).

[70] Parr, S. W., and Olin, H. L., *J. Soc. Chem. Ind.*, **32**, 589 (1913).

their vacuum tar. Schneider [64] reported no bases from brown coal up to 450° C but found them above that temperature. In a very detailed study of the distribution of coal nitrogen in low-temperature carbonization Fischer and Gluud [71] found one-third liberated, but mostly as free nitrogen and very little as ammonia. Gluud and Breuer [13] went into more detail and found that the nitrogen distribution, calculated on the basis of the coal nitrogen, was as shown in Table II. The 16.5 percent unaccounted

TABLE II

NITROGEN DISTRIBUTION IN PRODUCTS OF COAL CARBONIZATION, ON THE BASIS OF THE NITROGEN IN THE COAL [13]

	Percent
In the semicoke	66.1
As ammonia	1.8
As pyridine	0.4
In tar	4.4
In the gas as free nitrogen	10.8
Total	83.5

for was traced to the inaccuracies of the methods for determining nitrogen in coal and coke. The authors pointed out expressly that the nitrogen in the gas was actually determined and not obtained by difference, as is usual. Fritsche,[72] in an exhaustive study of the gases given off during low-temperature carbonization, did not even mention ammonia or pyridine, so their absence may be presumed. Wellington and Cooper [73] in their book on low-temperature carbonization claimed an average production of 18 pounds ammonium sulfate per ton of coal and gave figures from 12 to 26 pounds for well-known low-temperature

schemes. Gluud [58] definitely stated that no cyanogen is formed at low temperatures, and Porter [74] reported that "NH_3 is not formed appreciably below 500° C."

As carbonization temperatures go up the yields increase, especially that of ammonia. Roberts [75] aptly summarized the situation when he gave as average yields 12 pounds ammonium sulfate below 600° C, 15 pounds at 750° C, and 30 pounds above 900° C. Many of the so-called low-temperature carbonization processes actually operate at medium temperatures of 600 to 700° C, a fact that explains the often-claimed high ammonia yields of these processes. Since low-temperature carbonization has never become a real commercial success there is no need for a detailed accounting of such processes, and the reader is referred to books such as that of Wellington and Cooper [65] for yield figures on ammonia and other nitrogen compounds.

The tremendous influence of temperature on the release of coal nitrogen is properly illustrated by a number of important investigations, some of which are summarized in Tables III to VI.

TABLE III

INFLUENCE OF TEMPERATURE ON DISTRIBUTION OF NITROGEN IN CARBONIZATION PRODUCTS [76]

(Percentage of Coal Nitrogen)

Temperature, °C	600	700	800	900
In the coke	72.4			62.1
				Less than
As ammonia	10.6	19.6	21.0	21.0
As cyanogen and in tar	11.87	2.3	....	.
As free nitrogen	5.13	8.0	....	15.6

71 Fischer, F., and Gluud, W., *Ges. Abhandl. Kenntnis Kohle,* **3,** 213–6 (1918).

72 Fritsche, W., *Ges. Abhandl. Kenntnis Kohle,* **6,** 450–500 (1921).

73 Wellington, S. N., and Cooper, W. R., p. 54 of ref. 65.

74 Porter, H. C., p. 97 of ref. 18.

75 Roberts, J., *Coal Carbonization, High and Low Temperature,* Sir Isaac Pitman and Sons, London, 1927, p. 76.

76 Mayer, M., and Altmayer, V., *J. Gasbeleucht.,* **50,** 25–31 (1907).

TABLE IV

INFLUENCE OF TEMPERATURE ON THE DISTRIBUTION OF NITROGEN IN CARBONIZATION PRODUCTS [43]

(Taking as 100 Percent the Nitrogen Content of the Dry Ash-free Coal)

Temperature °C	As Ammonia percent	As Hydro-cyanic Acid percent	In Tar percent	As Free Nitrogen in Gas percent	In Coke percent
A. *Upper Silesian Coal* (1.396 percent nitrogen)					
(*a*) Size, 2½ mm					
600	7.81	0.25	2.12	18.13	71.69
700	18.13	0.66	3.65	12.13	65.43
800	21.28	0.87	3.47	10.73	63.65
900	24.12	1.19	4.15	12.14	58.40
1,000	23.15	1.23	5.11	21.53	49.98
1,100	23.09	1.31	3.70	30.51	41.39
1,200	22.84	1.42	4.21	45.10	26.43
(*b*) Size, 6-10 mm					
850	23.75	1.11	3.62	15.67	55.95
900	24.19	1.23	3.47	16.81	54.30
1,000	22.69	1.26	3.39	23.79	48.87
B. *Westphalian Coal* (1.391 percent nitrogen)					
Size, 2-2½ mm					
800	19.46	0.76	1.92	5.88	71.98
850	22.14	1.10	1.77	4.93	70.06
900	19.94	1.11	1.61	9.99	67.35
1,000	19.61	1.25	1.87	21.54	55.73
C. *Lower Silesian Coal* (0.965 percent nitrogen)					
Size, 2 2½ mm					
850	24.74	1.49	2.63	4.56	66.58
900	26.95	1.61	2.73	5.04	63.67
1,000	25.49	1.87	2.60	15.71	54.33

TABLE V

YIELD OF AMMONIA AS A FUNCTION OF THE CARBONIZATION TEMPERATURE [77]

(In Percent of the Coal Carbonized)

Temperature, °C	Laboratory Carbonization						Works Carbonization
	400	500	600	700	800	900	900–950
South Yorkshire coking coal	0.022	0.035	0.149	0.398	0.432	0.442	0.32
Durham coking coal	0.015	0.071	0.130	0.230	0.391	0.473	0.31
South Wales coking coal	.....	0.038	0.128	0.292	0.316	0.346	0.25

[77] Foxwell, G. E., *Fuel*, **3**, 227–35 (1924). Wigginton, R., *Coal Carbonisation*, Baillière, Tindall and Cox, London, 1929, p. 108.

TABLE VI

CONCENTRATION OF AMMONIA IN AQUEOUS DISTILLATE AS A FUNCTION OF CARBONIZATION TEMPERATURE [78]

Temperature, °C	400	450	500	550	600	650	700
Ammonia in grams per liter of aqueous distillate	1.24	2.27	3.23	6.61	12.06	11.64	15.68

High-temperature carbonization processes operating at, say, above 900° C, give the maximum conversion of coal nitrogen to useful compounds and, since they are vastly preponderant in the industrial set-up, will be considered primarily. Conversions which have been reported for normal carbonization are summarized in Table VII. Indi-

Very little information is available on the actual production of pyridine, chiefly because of the lack of interest in this product which prevailed in the past. Another reason is the fact that so far pyridine has been recovered almost exclusively from tar, though substantial quantities are contained in the gas and may be recovered from am-

TABLE VII

DISTRIBUTION OF NITROGEN IN THE PRODUCTS OF NORMAL CARBONIZATION

(In Percent of Coal Nitrogen)

Author	In the Coke	As Ammonia	As Cyanogen	In the Tar	As Free Nitrogen (by difference)
Foster [79]	48.68	14.50	1.56	....	35.26
Knublauch [3]	31–36	10–14	1.5–2	1.0–1.3	.....
Knublauch [80]	.....	12–14	2	1.33	.....
McLeod [7]	58.3	17.1	1.2	3.9	19.5
Short [29]	43.31	15.16	1.43	2.98	37.12
Heckel [35]	.....	11–25	1.6–4.4	....	.....
Stone [81]	46.30	13.05	1.42	....	39.23

vidual ammonia yields, especially as influenced by the type of raw material and carbonizing equipment, are shown in Table VIII in pounds of ammonium sulfate per ton of coal.

The practical yields of hydrocyanic acid have been reported to range from 0.62 to 1.96 pounds per ton of coal.[6, 82]

monia liquor, from the saturator operation, and from the light oil, depending on the plant set-up. Since light oil, tar, and ammonia liquor are dealt with in Chapters 28, 31, and 32, the present discussion will be confined to the gaseous phase. Recovery from the gas has become of importance through the opening up of new outlets for pyridine bases whose needs cannot be supplied by production from tar alone.

Klempt and Röber [83] have made a thorough study of the recovery of pyridine from

[78] Sinnatt, F. S., King, J. G., and Linnell, W. H., J. Soc. Chem. Ind., 45, 385–93T (1926).

[79] Foster, W., J. Gas Lighting, 40, 124–6, 1081–2 (1882); J. Chem. Soc., 43, 105–10 (1883).

[80] Knublauch, O., J. Gasbeleucht., 38, 769–73, 753–7 (1895); J. Soc. Chem. Ind., 15, 106 (1896).

[81] Stone, C. H., Gas Age-Record, 51, 241–3 (1923).

[82] Parrish, P., Gas J., 144, 413–20 (1918). Anon., Chem. Age, 1, 90–2 (1919). Espenhahn, E. V., Chem. & Met. Eng., 26, 938–41 (1922).

[83] Klempt, W., and Röber, R., Chem. Fabrik, 13, 65–8 (1940); Ind. Chemist, 16, 159 (1940).

TABLE VIII

Yields of Ammonium Sulfate Obtained Commercially

(In Pounds per Ton of Coal)

Author	Gas Works	Horizontal Retorts	Coke Ovens	Vertical Retorts	Steamed Verticals	Blast Furnaces	Unspecified Equipment	Coal Percent Nitrogen
Drehschmidt [8]							3.6–28.2	
Anderson and Roberts [15]	22.4		19.7			20.2		1.4
Rau [16]	9.6–24.0							
Short [29]		18		24.1				
Foster [79]							26.4	1.6
Knublauch [80]							3.8–57.8	1.3–1.6
Stone [81]				17.7				1.75
Leybold [84]							7.3–21.7	1.0–1.5
Henderson [85]				43 (shale)				
Truchot [86]						18–27.2		
Peters [87]			28.0–29.4				26.4–39.4	
Peters [88]			19.2–30.6					
Bolz [89]				26			20.8	
Ott [90]		20.8		19.6	19.2			
Gray [91]							20–36	
Curphey [92]							17.5–18	

ammonia saturator exhausts (indirect process). For a coke-oven plant producing 9,890,000 cubic feet of gas per day they found 138.2 pounds of pyridine bases in the raw gas. About 40 percent of the total production was precipitated with the tar, the remaining 60 percent passing on with the gas. These figures of Klempt and Röber would indicate a total production of 0.154 pound per ton of coal. According to unpublished private information one Amer-

ican plant recovers about 0.159 pound per ton for a coal of 33 percent volatile-matter content, and another plant [93] obtains about 0.16 pound per ton for a coal of 31 percent volatile-matter content. Thus yields of European and American practice are just about the same. Porter [94] aptly summarized the conversion of coal nitrogen in high-temperature carbonization graphically as shown in Fig. 1.

Simmersbach [43] concluded from his studies that the formation of ammonia takes place mainly at a temperature at which the coking of the coal is completed, i.e., from 800 to 900° C. Hilgenstock [95] pointed out that the main ammonia production occurs only after the completion of the coal-fusion process. Damm and Kor-

[84] Leybold, W., *Dinglers Polytech. J.*, **265**, 218 22 (1887); *J. Soc. Chem. Ind.*, **6**, 652 (1887).

[85] Henderson, N. M., *ibid.*, **16**, 984–90 (1897).

[86] Truchot, P., *Z. angew. Chem.*, **11**, 263–5 (1898).

[87] Peters, A., *J. Gasbeleucht.*, **51**, 1114–8 (1908).

[88] Peters, A., *ibid.*, **51**, 465–71 (1908).

[89] Bolz, Chr., *ibid.*, **52**, 591–6 (1909).

[90] Ott, E., *ibid.*, **52**, 621–6 (1909).

[91] Gray, T., *Am. Gas Light J.*, **105**, 38–9 (1916).

[92] Curphey, W. S., *Gas J.*, **151**, 179–80, 234–7 (1925); *Gas World*, **73**, 83–6 (1920).

[93] Courtesy of F. D. Schreiber of Pittsburgh Coke and Iron Co.

[94] Porter, H. C., p. 331 of ref. 18.

[95] Hilgenstock, G., *J. Gasbeleucht.*, **45**, 617–21 (1902).

ten [96] found that 85 percent of the ammonia was evolved after the coke set. This contention is proved by the work of Gluud and Breuer,[13] who found that a coal which on low-temperature carbonization had given only about 10 percent of its normal ammonia yield released another 90 percent when
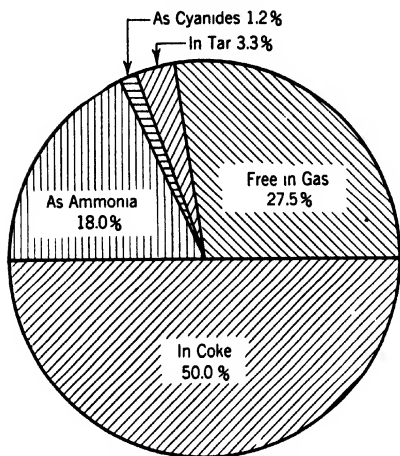
Fig. 1. Distribution of coal nitrogen in carbonization products.[94]

the semicoke was heated to a higher temperature.

There are a number of other factors, besides temperature, which may or may not have some bearing on the ammonia and cyanogen production in coking operations. One is the particle size. Whereas Simmersbach [43] found no appreciable effect, Douglas and Jones [97] noticed an increase of 5 pounds of ammonium sulfate per ton of coal when it was coked uncrushed, 3-inch size and under. Foxwell,[98] on the other

hand, found an increased yield with decreased particle size.

A rather unexpected influence on ammonia yield was found by Christie [99] to reside in the speed of carbonization. A slow heating to the same end temperature (865° C) increased the yield, as may be seen from Table IX.

TABLE IX

INFLUENCE OF SPEED OF CARBONIZATION ON YIELD OF AMMONIA [99]

(In Percent of Coal Nitrogen)

Time, minutes	In Coke	As Ammonia	Otherwise Volatized
12	66.42		33.58
80	56.92	18.25	24.83
170	37.35	27.45	35.20

Another factor of great importance is the age of the coal used. One might assume that ammonia production would be roughly parallel to the nitrogen content of the coal. Though this view was maintained by Leybold [84] it was disputed by Knublauch,[80] and general practice would tend to support Knublauch. McLeod [7] was probably the first to observe that coals with high coke yield retained more nitrogen in the coke than coals giving a lower coke yield. Thus high-volatile coals should give substantially more ammonia than low-volatile ones. This is borne out by Table X by Porter,[100] who

TABLE X

YIELDS PER TON OF COKE ON VARIOUS MIXTURES OF PITTSBURGH (HIGH-VOLATILE) AND POCAHONTAS (LOW-VOLATILE) COALS

(17-hour coking time, 18-inch oven) [100]

Percent Pittsburgh in mix	20	40	60	80	100
Percent Pocahontas in mix	80	60	40	20	0
Yields per ton of coal, pounds of ammonium sulfate		17.0	19.0	21.5	24.0	26.0

96 Damm, P., and Korten, F., *Glückauf*, **67**, 1339–45 (1931).

97 Douglas, A. S., and Jones, C., *Gas World*, **67**, Coking Sect., 10 (1917).

98 Foxwell, G. E., *Fuel*, **3**, 22–8 (1924).

99 Christie, M. G., dissertation, Aachen, 1905.

100 Porter, H. C., p. 410 of ref. 18.

attributed the result [101] to the protective action of the larger amount of water and carbon dioxide given off by high-volatile coals. This is substantiated by the investigations of Kattwinkel,[102] who found that especially oxidized coals yield more ammonia on coking. Rau [16] showed that not only does the ammonia yield decrease with increasing coke yield but so also do the yields of cyanogen and nitrogen in tar. The same author gave the data shown in Table XI, which demonstrates the influence of the oxygen content of coals on their ammonia yield.

little if any free iron oxide for contact with the gas.

(5) Full charges, or a practical minimum of space left unoccupied in oven or retort above the charge.

(6) Uniform heats, rendering unnecessary the overcoking of some parts.

(7) Steaming of the charge during the last fifth of the carbonizing period, that is, after all of the raw coal has passed through the plastic stage.

(8) Use of coal, in admixture, of a type bearing as high a percentage of oxygen as will not interfere with requisite quality in coke or gas.

But, with the best practice of plant operation, the actual recovery of coal nitrogen

TABLE XI

INFLUENCE OF OXYGEN CONTENT OF COAL ON THE AMMONIA YIELD [16]

Oxygen in the coal, percent	32.60	12.66	12.46	10.76	9.09	5.04
Ammonia in percent of total nitrogen	35.23	10.98	20.83	23.07	13.92	9.96

Industry on the whole has been very conscious of these factors which influence ammonia yield, and a number of writers [29, 35, 39, 97, 103] have made general recommendations for proper plant operation to secure the highest recovery. Such advice has also been given, particularly for American practice, by Porter,[104] as follows:

(1) Maintenance of oven top space as cool as is compatible with efficient practical coke production.

(2) Avoidance of the leakage of air into the ovens which would effect combustion and raise locally the temperature of the gases.

(3) Avoidance of too rapid a coking rate with the high temperatures necessary thereto.

(4) Use of coals with a minimum of iron in their ash, and of refractories presenting

in the form of useful products is still sadly short of what should be possible if all the coal nitrogen could be converted. Quite naturally people have made efforts to boost the ammonia yield by artificial means. Nothing has been done to boost the yields of cyanogen or pyridine, and here may be a fruitful field for further research, especially in view of the increasing demand for pyridine and its homologs.

Inorganic additions to the coal were tried very early, lime being prominent among them. This was probably an unconscious adaptation of the old soda-lime method for determining nitrogen. Knab [105] was perhaps the first to propose it, but Cooper [106] is usually given the credit. Wanklyn [107] reported in detail on the Cooper process and claimed to have obtained increases in am-

[101] Porter, H. C., p. 333 of ref. 18.

[102] Kattwinkel, R., *Glückauf*, 63, 160–5 (1927).

[103] Jones, L. C., *J. Ind. Eng. Chem.*, 3, 589–94 (1911). Anon., *Am. Gas Eng. J.*, 111, 223–5 (1919). Plenz, F., *Gas- u. Wasserfach*, 66, 97–9 (1923); *Am. Gas J.*, 119, 29–32 (1923). Seelkopf, K., *Glückauf*, 66, 989–93, 1029–36 (1930).

[104] Porter, H. C., p. 332 of ref. 18.

[105] Knab, D. C., *Ber.*, 8, 180 (1875); Brit. Pat. 2,482 (1873).

[106] Cooper, W. J., Brit. Pat. 5,713 (1882).

[107] Wanklyn, J. A., *J. Soc. Chem. Ind.*, 2, 438–40 (1883).

monia yield of 20 to 35 percent. In a later paper,[108] the same author claimed that the yield was boosted from a customary 6 pounds of ammonia to 17 pounds, but he admitted that in two gasworks no gain was noted. He pointed out that grinding of the coal and good mixing were essential to the success of the process.

Knublauch [109] in a large series of laboratory tests, which he carefully corrected by empirical factors for plant practice, found that lime addition increased the ammonia yield by 20 percent, and silica addition increased it somewhat less. However, Knublauch pointed to serious disadvantages: increase in ash content of the coke, lowering of its heating value, production of lower-Btu gas, and reduction in tar yield. Anderson and Roberts [15] reported that some gasworks increased their yields of ammonia by 20 to 36 percent, although others got no increase. They reported also on the influence of sodium hydroxide and sodium carbonate; the hydroxide was said to have eliminated the nitrogen almost completely from noncoking coals but to have had no effect on coking coals. Mayer and Altmayer [76] obtained yield increases of 20 percent. Hahn, as reported by Rau,[16] contended that the addition of lime to coal did not reduce the nitrogen in coke but merely split the tar bases with liberation of ammonia. Barber,[110] in practical gasworks experience with coal liming, found an ammonia increase of 11 percent, a doubling of cyanogen production, no deleterious effect on the coke, and a number of operating advantages. He used a lime addition of 2 percent. Patterson [111] also spoke in a laudatory manner about the process, mentioning

an ammonia gain of 1.9 pounds over the average of the preceding seven years, higher gas yields, smoother plant operation, less sulfur in the gas, no impairment of the coke quality, but a lessened tar yield.

Though these investigations belong to the past and the process is probably dead, to-day the problem is still alive. Later writers have taken it up and viewed it from different angles. Eastwood [112] added lime, calcium carbonate, and iron oxide to coal, and carbonized in atmospheres of nitrogen, hydrogen, and nitrogen-steam mixtures. In nitrogen, lime and calcium carbonate increased the yield of ammonia, and iron oxide decreased it; in hydrogen, lime and calcium carbonate increased the yield, and iron oxide was without effect; and in nitrogen-steam mixtures, all three additions produced higher yields, lime being the most effective. Parker, Kerr, and Marson [113] found that calcium carbonate, sodium carbonate, and iron oxide increased the yield at 920° C but decreased it at 815° C.

An interesting, though hardly practical, attempt to increase ammonia yield was made by Ostwald and Riedel,[114] who added salts containing water of hydration, in particular calcium or magnesium chloride, to coal before charging to coke ovens or to coke going into producers and blast furnaces. They claimed to have obtained the total nitrogen of the coal or coke in the form of ammonium chloride.

Almost contemporary with the lime process was another proposal to increase ammonia yield: the use of hydrogen. Tervet [115] claimed that on passing hydrogen

[108] Wanklyn, J. A., *ibid.*, **3**, 12–5 (1884).

[109] Knublauch, O., *J. Gasbeleucht.*, **30**, 55–61, 96–101 (1887).

[110] Barber, C. C., *J. Gas Lighting*, **116**, 765 (1912).

[111] Patterson, J., *ibid.*, **116**, 449–53 (1912).

[112] Eastwood, A. H., *Gas J.*, **192**, 745 (1930).

[113] Parker, A., Kerr, H., and Marson, C. B., *Trans. Inst. Gas Engrs.*, **78**, 240–8 (1928–9), **79**, 50–103, 143–55 (1929–30).

[114] Ostwald, W., U. S. Pats. 1,386,723 (1921), 1,526,178 (1925). Riedel, A., Ger. Pat. 298,603 (1922); Brit. Pat. 102,146 (1916).

[115] Tervet, R., *J. Soc. Chem. Ind.*, **2**, 445–49 (1883); Brit. Pat. 1,842 (1883).

over hot coke up to 83 pounds of ammonium sulfate per ton of coal could be obtained. He also found mixtures of carbon dioxide and hydrogen and of hydrogen and steam to work, but not methane or mixtures of carbon dioxide and nitrogen. Tervet further pointed out that coke which yields no hydrogen on heating will not yield additional ammonia if hydrogen is passed over it; the more hydrogen released on heating, the more ammonia will be obtained by passing hydrogen over it. If this warning had been heeded by later investigators, unnecessary controversies would have been avoided. Beilby [116] repeated Tervet's work and in general agreed with him. Rau [16] quoted Salm as having been unable to check Tervet's observations. Cobb [45] checked Tervet, at least to some extent. It remained for Monkhouse and Cobb [117] to show that the Tervet reaction will go with a 500° C coke but not with a 1,100° C coke. Seemingly, then, Tervet's reaction is a straight hydrogenation and does not depend on a protective action of the hydrogen for ammonia. This is reasonable in the light of later experience, which has taught us that low-temperature coke can still be hydrogenated, but not high-temperature coke. Complete recovery of the coal nitrogen was obtained by Bergius and Billwiller [25] and Fischer and Tropsch,[26] and was reported by Fischer.[25] Researches which also belong here are those of Fischer and Keller,[118] who coked coal under hydrogen pressure up to 66 atmospheres and at temperatures of 500, 750, and 950° C. Unfortunately, because of the smallness of their samples they gave no quantitative data on ammonia production. Finally, Badanova and Gabinskii [119] coked coal under the pressure of its own gases, and found the yield of ammonia to go up with increasing pressure and temperature while the hydrogen content of the gases went down.

Steaming. By far the most fruitful and far-reaching proposal to boost artificially the conversion of coal nitrogen to ammonia was the use of steam. The protective action of steam has already been dealt with in this chapter, but mainly as concerned its effect on the thermal dissociation of ammonia. The steam has another function in liberating nitrogen from coke under conditions under which it otherwise no longer gives off nitrogen compounds.

Mayer and Altmayer [120] distilled coal at temperatures of 600 to 900° C for 3 hours, and then followed by 18 hours of steaming. The highly illuminating results shown in Table XII were obtained. It is readily seen that above 800° C the decomposition of ammonia becomes so formidable that the

TABLE XII

EFFECT OF STEAMING ON YIELD OF
AMMONIA [120]

	Time of Experiments, hours	Yield of Ammonia in Percent of Total Nitrogen at			
		600° C	700° C	800° C	900° C
Carbonization	3	10.83	19.17	21.38	20.57
Steam	6	13.04	20.85	23.12	23.84
	9	3.17	8.53	9.64	5.35
	12	1.84	5.10	6.12	2.21
	15	0.17	3.17	3.71	.....
	18	.....	1.50	2.14	.....
	21	.....	.....	1.12	.....
Total ammonia in percent of nitrogen in coal		29.05	58.32	67.23	51.97

116 Beilby, G. T., *J. Soc. Chem. Ind.*, **3**, 216–24 (1884).

117 Monkhouse, A. C., and Cobb, J. W., *Gas J.*, **156**, 234–40 (1921), **158**, 828–33 (1922); *Gas World*, **75**, 337–43 (1921); *Iron & Coal Trades Rev.*, **103**, 582–4 (1921); *Brennstoff-Chem.*, **4**, 218–9 (1923); *Trans. Inst. Gas. Engrs.*, **20**, 137–58 (1922); *Fuel*, **1**, 177–9 (1922).

118 Fischer, F., and Keller, K., *Ges. Abhandl. Kenntnis Kohle*, **1**, 148–54 (1915–6).

119 Badanova, Z. I., and Gabinskii, Y. O., *Novosti Tekhniki*, **1937**, No. 24, 35–6.

120 Mayer, M., and Altmayer, V., *J. Gas beleucht.*, **50**, 49–54 (1907).

increased liberation due to the steam is overshadowed and the overall yield drops. In its stead an increased yield of free nitrogen was noted by the authors, so that ammonia probably was originally liberated as would be expected. Cobb [45] passed various gases over coke at 800° C, obtaining substantially no ammonia with carbon dioxide, carbon monoxide, or nitrogen. He got 10 percent of the coke nitrogen as ammonia when he used hydrogen, and practically all of it with steam.

Salmang [121] investigated some ramifications of this problem, especially the percentage conversion to ammonia of the nitrogen contained in various fuels, at a number of temperatures, using steam or mixtures of steam and air. He also tested the influence in this reaction of various catalysts, such as calcium carbonate and ferric oxide. In the straight water-gas reaction he found the results shown in Table XIII.

TABLE XIII

YIELDS OF AMMONIA OBTAINED IN THE WATER-GAS REACTION [121]

Temperature, °C	Grams Steam per Gram Gasified Carbon	Ammonia in Percent of Eliminated Nitrogen
1,050	Much	35.9
1,100	62.5	8.4
1,100	191.1	10.3
1,100 plus 5% CaCO₃	38.0	27

The "mixed-gas" reaction (steam and air) as influenced by catalysts gave at 900° C the results shown in Table XIV. The influence of the nature of the coals and the addition of lime on the ammonia yield in the steam-air gasification process at 900° C

TABLE XIV

YIELDS OF AMMONIA OBTAINED AT 900° C ON GASIFICATION WITH STEAM AND AIR [121]

Addition	Per Grams Gasified Carbon		Ammonia in Percent of Eliminated Nitrogen
	grams steam	liters air	
0	76.1	2.80	59.0
5% CaCO₃	49.1	8.24	62.8
5% CaCO₃	42.0	5.78	96.3
5% Fe₂O₃	21.6	7.18	70.0
0	7.3	8.91	7.9
5% CaCO₃	37.5	9.47	16.1

is seen from Table XV, in which the figures mean percentage conversion of the eliminated nitrogen to ammonia.[121] Salmang concluded with the significant statements that the ammonia formation progresses uniformly with carbon combustion throughout the whole gasification process; that the ratio of carbon to nitrogen remains the same throughout; and that therefore the nitrogen is tied to the carbon and cannot be liberated without the carbon.

TABLE XV

PERCENTAGE CONVERSION OF ELIMINATED NITROGEN TO AMMONIA FOR VARIOUS COALS ON GASIFICATION WITH STEAM AND AIR [121]

Coal	Without Lime	With Lime
Brown coal briquets	95	95
Young high volatile	82	86
High volatile	78	85
Medium volatile	88	96
Medium-volatile briquets	82	81
Low-volatile briquets	73	84
Anthracite	82	94

Sachs, as cited by Terres,[11] used his "hot-cold tube" principle in the mixed gas reaction at 800° C and obtained 87 percent of the coke nitrogen as ammonia. Fischer and Gluud [71] gasified low-temperature coke with steam at "above 575° C" and converted 94 percent of its nitrogen content to ammonia. Monkhouse and Cobb [117] prepared cokes

121 Salmang, H., dissertation, Aachen, 1914; Z. angew. Chem., 28, 624 (1915), 32, 148 (1919). Markgraf, H., Stahl u. Eisen, 35, 905-8 (1915).

at 500° C (soft), 800° C (medium), and 1,100° C (hard), and treated them with nitrogen, hydrogen, and steam singly, in mixture, and successively. Treating soft coke at 800° C first with nitrogen, then with hydrogen, and finally with steam yielded a total of 79.2 percent of the nitrogen in coke as ammonia. The same coke treated with hydrogen only, but at 1,000° C, gave 68 percent as ammonia; a treatment with nitrogen plus steam at 800° C gave 98.3 percent of the nitrogen as ammonia. The hard coke yielded only to prolonged action of steam, and nitrogen and hydrogen did not do very much. At 1,000° C this hard coke gave up in a steam-nitrogen current 97.3 percent of its nitrogen as ammonia. Pexton and Cobb [44] confined themselves to the gasification of coke with steam, and their results are therefore much more clear-cut. They used 800° C (A) and 1,100° C (B) laboratory coke and byproduct oven coke (C). When coke A was gasified there was at first a preferential elimination of nitrogen, for the ratio of carbon to nitrogen increased; later on it remained constant. When gasified at 900° C in an amount of steam similar to that used in a water-gas generator, little ammonia survived dissociation, but trebling the amount of steam resulted in almost complete recovery of the nitrogen as ammonia. At 950° C, coke A gasified with twice the velocity with which it gasified at 900° C. From 60 to 70 percent of the eliminated nitrogen was recovered as ammonia. Treatment at 1,000° C, even with a large excess of steam, yielded little ammonia. Cokes B and C when gasified at 900° C with liberal amounts of steam yielded the same amounts of ammonia. The authors came to the same conclusion as Salmang, namely, that carbon and nitrogen are "gasified" at the same rate and that the ratio of carbon to nitrogen in the residue remains constant throughout the gasification.

Application of the steaming principle to coal carbonization has been advocated repeatedly. Kenyon [122] proposed it for gas-house retorts and claimed to have recovered 90 percent of the coal nitrogen as ammonia. Tichauer [5] also wanted it used for gas retorts and especially for coke ovens. He claimed to have obtained 85 percent of the coke nitrogen as ammonia on steaming at 800 to 900° C. West [123] published the results for continuous vertical retorts with and without steaming which are shown in Table XVI. Mott [36] also favored steaming

TABLE XVI

YIELDS PER TON OF COAL IN VERTICAL RETORTS [123]

	Gas cubic feet	Coke pounds	Tar plus Light Oil gallons	Ammonium Sulfate pounds
Steamed	25,273	853	24.6	52.86
Not steamed	11,450	925	14.5	30.50

in coke-oven practice but wanted it confined to the last period of coking, from the twenty-second to the twenty-sixth hour. He pointed out the danger of affecting adversely the quality of coke and gas.

An intensive study of steaming in horizontal retorts was made by Krau.[124] By blowing steam at 0.05 atmosphere and 3 atmospheres pressure into the carbonizing coal he increased the ammonia yield by 8 to 17 percent and by 25 percent respectively. Superheated steam boosted the ammonia yield by 27 percent. Krau also blew steam or water gas into the free spaces of the retorts and thus increased the yield by

122 Kenyon, H., Brit. Pat. 1,016 (1886).
123 West, J., *Gas World*, **69**, 180 (1918).
124 Krau, K. F., *Gas- u. Wasserfach*, **65**, 531–2 (1922); *Gas J.*, **159**, 645 (1922).

dilution, cooling, and flushing action. He concluded that first-class water gas can be made in this manner with a simultaneous increase of the ammonia yields over the normal figures. Another interesting report comes from Braidwood,[125] who, like West, worked with vertical retorts. He considered heavy steaming with moderate retort temperatures essential for high ammonia yields. With 40 percent steaming he obtained 48.96 pounds of ammonium sulfate; with 20 percent steaming the yield fell to 39.52 pounds. The presence of large amounts of hydrogen was without influence, and the introduction of blue water gas was also without beneficial effect.

However, the most important application of the principle of increasing ammonia yield by steaming came with its introduction into the practice of complete gasification of solid fuels. Without doubt Mond is the man to be credited with it, though several earlier inventors laid the groundwork on which Mond was able to build his system. A large number of apparatus modifications have been described, but all are based on the principle that the fuel is completely gasified until only ash is left. This may be done in the presence of steam alone, using external heating, or of steam plus air, in which event the system is self-maintaining as far as its heat balance is concerned. Then, again, a separate carbonization may precede the gasification step, or the fuel may be carbonized in the same apparatus but before it reaches the gasification chamber. One of the reasons for these seeming complications is the desire to produce a high-Btu gas, which is possible only if the carbonization gases are collected separately. There is no thought of presenting all these apparatus modifications here, since they are dealt with in Chapters 36 and 37.

The first work on this subject was probably done by Beilby and Young,[126] who distilled oil shale and also coal, and treated the char with steam at considerably higher temperatures. They also mentioned the use of air with the steam. Their contemporary, Grouven,[127] steamed peat in vertical retorts, utilizing its natural moisture to furnish the steam, and burning part of the peat to furnish the necessary heat. On this foundation Mond [128] proposed his famous process, in which a restricted amount of air laden with steam is passed into the producer. His novelty was that the air was so restricted and so much steam was used that the fuel bed was only dark red and was maintained below the dissociation temperature of ammonia. In a later publication [42] Mond gave operating data from which it appears that 64 pounds of ammonium sulfate were recovered per ton of coal and that 2 tons of steam were used per ton of coal. Mond well realized that his scheme was profitable only for very large installations, since the gas produced was of low heating value and could be used only for centralized power generation on a very large scale. He recognized also that gasification with steam alone gave still greater ammonia yields, but he compromised on air plus steam because this mixture obviated practical difficulties of heating.

Young and Beilby [116, 129] later devoted themselves more to coal and also switched from steam to a mixture of steam and air; they have discussed in detail the relative

125 Braidwood, G., *Gas J.*, **163**, 180–9 (1923); *Gas World*, **78**, 637–46 (1923).

126 Beilby, G. T., Brit. Pat. 2,169 (1881); *J. Soc. Chem. Ind.*, **3**, 216 (1884). Young, W., Brit. Pat. 1,587 (1881); *J. Gas Lighting*, **40**, 257–8 (1882). Young, W., and Beilby, G. T., Brit. Pat. 5,084 (1882).

127 Grouven, H., Ger. Pats. 13,718, 18,051 (1881), 17,002 (1882).

128 Mond, L., Brit. Pat. 3,923 (1883).

129 Young, W., and Beilby, G. T., Brit. Pat. 1,377 (1882); *J. Soc. Chem. Ind.*, **4**, 472–4 (1885).

advantages of these systems. Seemingly, if steam alone is used the difficulties of heating are too great, and quantities of steam as high as 20 to 30 times the weight of the coal are required to counteract the destructive effect (on ammonia) of the high operating temperature (1,100° C). This obviously is impractical. By their modified process with steam and air they recovered as much as 60 to 80 percent of the coal nitrogen in the form of ammonia. Young and Beilby's conviction that a water-gas machine would not be a good apparatus for the gasification of fuels if high ammonia yields were desired is borne out also by an investigation of Pexton and Cobb,[130] who concluded that the production of high-grade water gas is unlikely under conditions which favor ammonia preservation.

The whole problem of gasification in Mond producers was studied intensively by the great nitrogen chemists Frank and Caro. They sponsored the gasification of mine refuse and high-nitrogen peat, on account of their cheapness, and tried to inaugurate a great program of power production and long-distance transmission, using the peat bogs as bases of operation. The ammonia, then highly valued and obtained in large quantities in the Mond process, was to have paid a considerable share of the expenses. A number of their patents and publications [8, 131] present many valuable ideas, particularly along economic lines. As an illustration of what can be expected of peat, some of their results are given in Table XVII.

Bone and Wheeler [132] made a thorough

TABLE XVII

YIELDS OF AMMONIA FROM GASIFICATION OF PEAT IN A MOND PRODUCER [131]

Percent nitrogen in the peat	1	1.05	1.6	2.8
Ammonium sulfate in pounds per ton of peat	56	80	118	220

study of a Mond gas plant. They found that the quality of gas was lowered with higher steam saturation temperature, and the overall efficiency also decreased. Unfortunately the ammonia production increased with increasing steam saturation temperatures, so that these two factors have to be balanced economically. Table XVIII shows the trend as found by Bone and Wheeler.

TABLE XVIII

EFFECT OF STEAM SATURATION TEMPERATURE ON YIELD OF AMMONIA IN A MOND GAS PRODUCER [132]

Steam Saturation Temperature, °C	Pounds Ammonium Sulfate per Ton of Coal
60	35.4
65	39.9
70	45.8
75	58.3
80	64.2

An interesting contribution was made by Sachs,[133] who passed the gases from a Mond producer through chilled tubes, whereby he succeeded in converting all the nitrogen in the fuel to ammonia.

A large number of papers and patents are available which deal with a variety of problems connected with the complete gasification of fuel in a manner more or less similar to the Mond process. These publications deal with descriptions of individual plants, special plant arrangements, eco-

130 Pexton, S., and Cobb, J. W., *Gas J.*, **167**, 161–9 (1924) ; *Gas World*, **80**, 675–8 (1924).

131 Frank, A., *Z. angew. Chem.*, **11**, 16–20 (1898), **20**, 1592–5 (1907), **21**, 1597–1600 (1908). Caro, N., *ibid.*, **19**, 1569–81 (1906) ; Brit. Pat. 13,669 (1907). Wahlen, C., and Caro, N., Brit. Pat. 13,668 (1907).

132 Bone, W. A., and Wheeler, R. V., *Metallurgie*, **4**, 321–41 (1907).

133 Sachs, K. P., *Stahl u. Eisen*, **35**, 801–10 (1915).

nomics of the process, special constructions of the producers in several stages, either to carbonize separately or to preserve the ammonia by cooling, etc. They will not be discussed but will merely be cited as references for those who want more detail.[5, 6, 10, 12, 134] From a number of these

TABLE XIX

YIELDS OF AMMONIA FROM MOND GAS
PRODUCERS [12, 135, 136]

	Percent Nitrogen in Coal	Pounds of Ammonium Sulfate per Ton of Coal
Peat	.....	86
Peats	1–2.3	62.4–187.6
Peat	1.59	48
Peat, Australia	2.8	225
Brown coal	0.7	35.6
Brown coal	1.23	39.4
Young bituminous	2.39	102.4
Bituminous		
Silesia	1.56	80.2
S. Africa	1.43	100
S. Africa	1.3	90
N. Europe	1.08	65
England	1.44	100
England	1.42	90–95
England	1.5	80.4–89.4
Coking bituminous	1.39	62.8
Bituminous culm	1.26	57.4
Semianthracite		
Westphalia	1.69	90.4
S. Africa	2.2	155

134 Kuntze, P., Ger. Pat. 62,589 (1892). Masons Gas Power Co. et al., Brit. Pat. 28,054 (1908). Von Keler, H., Z. angew. Chem., 22, 1396–406, 1445–51 (1909). Duff, A. B., Brit. Pat. 20,938 (1911); Gas World, 57, 601 (1913). Gwiggner, A., Stahl u. Eisen, 31, 2085–8 (1911). Schulz, R., ibid., 33, 1221–5 (1913). Roser, E., ibid., 40, 387–95, 349–57 (1920). Fischer, F., Ges. Abhandl. Kenntnis Kohle, 6, 501–22 (1921). Van Ackeren, J., U. S. Pat. 1,375,475 (1921).

135 Ekenberg, M., J. Soc. Chem. Ind., 28, 511–2 (1909). Haber, F., J. Gasbeleucht., 53, 421–4 (1910). Lazar, O., J. S. African Assoc. Anal. Chem., 4, 13-27 (1921); Chem. Abs., 15, 1801 (1921).

136 Rambush, N. E., J. Soc. Chem. Ind., 40, 293–300T (1921).

references, Table XIX has been computed which shows the ammonia yields obtained from coals of different ages and different nitrogen contents, in producers more or less of the Mond type.

From the old Mond producer there was a gradual transition to modern machines in which much less steam is used. Though this normally means lower ammonia production, much can be accomplished by proper design of the equipment. Rambush [136] emphasized that in the producer with which he worked only 1 to 1.5 pounds of steam were used per pound of coal, in contrast to the 2.5 pounds in a regular Mond producer, but the same amount of ammonia was recovered. Ovitz [137] reported on a producer in which Pittsburgh Seam coal with 1.5 percent nitrogen was employed. The steam consumption was 1 pound per pound of coal, and 22.11 pounds of ammonium sulfate per ton of coal were recovered.

Very little is known about cyanogen or pyridine in producers and water-gas machines. The only indications are the assertions by Trenkler [12] that the presence of cyanogen compounds in producer gas has not yet been proved, and by Taplay and Parkinson [138] that, in equipment in which steaming is employed, hydrogen cyanide is converted to ammonia. Since even in coke-oven gas cyanogen compounds occur only in small quantities, their recovery from these sources, if they are there at all, would be of very doubtful economic merit, on account of their dilution by very large gas volumes.

The remaining piece of apparatus in which fuel is used and from which nitrogen compounds may be recovered is the blast furnace. It is not often considered,

137 Ovitz, F. K., Chem. & Met. Eng., 21, 253–5 (1919); Chem. Eng., 27, 239–41 (1919).

138 Taplay, J. G., and Parkinson, B. R., Gas World, 70, 451–4 (1919); Gas J., 146, 622–4 (1919).

because coke is the usual fuel and its nitrogen content would normally not be released as ammonia under the conditions of the blast furnace, except in quantities which would be difficult to recover from the large volumes of blast-furnace gas. However, Scottish blast furnaces have long been fueled with splint coal, and ammonia was recovered from them at an early date. Scotch splint coal, according to Jones,[139] contains 1.35 percent nitrogen and would yield 142.5 pounds of ammonium sulfate, if all of it could be converted to ammonia and recovered; actually, 24 to 29 pounds was obtained. An anonymous report[140] gave the yield figure as 22.6 pounds per ton of coal. That this source of ammonia has been of considerable economic importance, at least in the past, may be seen from the ammonium sulfate production figures for Great Britain of the year 1898, which were given by Anderson and Roberts[15] and shown in Table XX. An historical survey of the recovery of byproducts from blast-furnace gas was given by Hamilton.[141]

In concluding this part of the chapter it may be well to point out that the efforts of the workers in this field have been directed, not only toward increasing the yield of ammonia and preserving it, but also toward retrieving that portion of it which under normal circumstances (e.g., in coke ovens) is converted to cyanogen. Inasmuch as about 10 percent of the ammonia yield is usually lost in this fashion, such efforts are quite understandable. All the proposed schemes are based on the fact that hydrogen cyanide is a nitrile and can, as such, be hydrolyzed to ammonia and carbon monoxide or dioxide. The older processes, which are fewer in number, are based on the use of steam at high temperatures. Dunnachie[142] advocated withdrawal of cyanogen-containing gases from the hotter regions of blast furnaces, gas producers, coke ovens, etc., and their treatment with steam outside the gas-producing furnace. Collin[143] proposed substantially the same thing, though he first removed the ammonia already contained in the gas by an acid wash and sometimes used sulfuric acid with the steam to aid hydrolysis. Halvorsen[144] added hydrogen and air (to form the necessary steam) to the gas and passed it over an iron-chromium catalyst at 400° C. He claimed a 99 percent conversion. Bähr,[145] in the course of his gas purification process, also passed the cyanogen-containing gases over catalysts at elevated temperatures and converted the cyanogen to ammonia. The second group of processes recover cyanogen in the form of ammonium thiocyanate, which in its turn is then hydrolyzed to ammonia.

TABLE XX

PRODUCTION OF AMMONIUM SULFATE IN GREAT BRITAIN IN 1898[15]

	Tons
Gasworks	129,590
Shale-oil works	37,264
Blast furnaces	18,000
Coke ovens	11,568

RECOVERY AND UTILIZATION OF AMMONIA FROM GASES

Coal carbonization is the principal source of ammonia, and it serves excellently to il-

[139] Jones, W., J. Soc. Chem. Ind., **4**, 737–8 (1885).

[140] Anon., Stahl u. Eisen, **16**, 381–3 (1896).

[141] Hamilton, R., J. Soc. Chem. Ind., **35**, 663–5 (1916).

[142] Dunnachie, W. J., Brit. Pat. **10,805** (1907); Ger. Pat. 215,532 (1909).

[143] Collin, F. J., A.-G., Brit. Pat. **145,696** (1920).

[144] Halvorsen, B. F., U. S. Pat. **1,580,038** (1926).

[145] Bähr, H., Ger. Pat. **567,631** (1933).

lustrate the conditions usually encountered and the methods employed in the recovery and utilization of ammonia from gases. For a historical outline of ammonia recovery from shale distillation, producer gas, and blast-furnace gas, Lunge-Köhler [4] may profitably be consulted. The basis for all recovery methods is the great solubility of ammonia and its salts in water, and its basic nature, which allows easy combination with acids and acidic materials.

As the hot carbonization gases come from the ovens or retorts, they are laden with water and tar vapors, in which the ammonia is contained as free ammonia and in the form of salts such as ammonium chloride, the last dissociated into ammonia and free hydrogen chloride as long as the temperature is high enough. The crude gas is precooled by spraying cool tar and

ammonia liquor into the collecting main. From this point on the methods differ. The oldest one, which was developed in gasworks, is still extensively used in Europe, although it never became prominent in America. The gas, after its preliminary cooling in the collecting main, is cooled in indirect tubular coolers with the aid of air, or more usually water. In this process more tar and water vapor are condensed, the water carrying with it some ammonia and almost all the ammonium salts. Part of this condensate is used in the collecting main as the primary cooling medium. After the primary cooler, the gas is freed from tar fog in special tar separators and then enters a series of scrubbers, in which it is washed countercurrently and directly with weak ammonia liquor and finally with fresh water. The relatively clean, cool gas
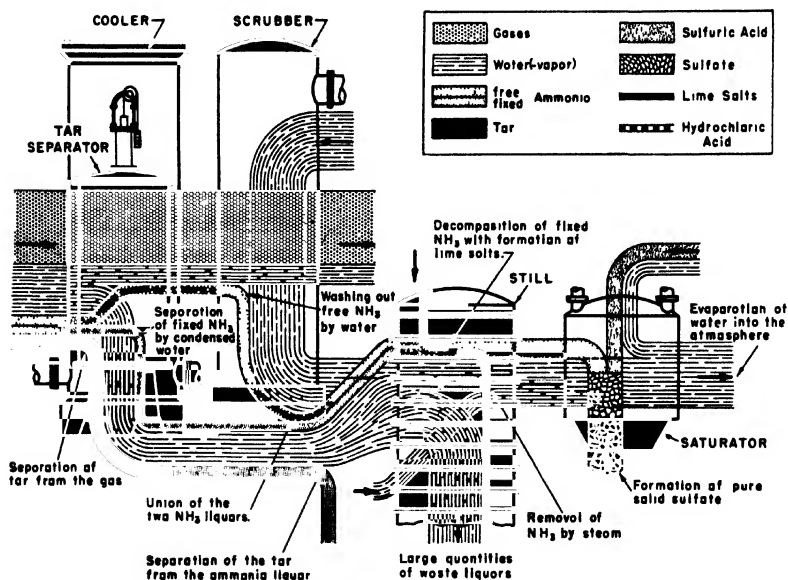
FIG. 2. "Indirect" process for recovery of ammonium sulfate.[147]

then passes on to be freed of benzol and similar hydrocarbons, and of hydrogen sulfide, hydrogen cyanide, etc. The various aqueous condensates, called ammonia liquors, are united. They contain free ammonia; ammonia in the form of easily dissociated salts, such as carbonate, bicarbonate, sulfide, hydrosulfide, cyanide; and ammonia in firmer bond (so-called fixed ammonia) such as chloride, sulfate, sulfite, thiosulfate, thiocyanate. The more volatile

pyridine bases are also to be found in the ammonia liquor to a considerable extent, though the larger part remains in the tar Since ammonia liquor is dealt with in detail in Chapter 32 it will not be treated here except in following the path of the ammonia.

In order to recover ammonia from this liquor it is heated in a still with steam, which drives out the free ammonia and such ammonia as can be obtained by their-

SATURATOR

Tar becomes acid in the saturator.

Tar goes into saturator liquor

Formation of HCl from the fixed NH₃

Gases	Sulfuric Acid
Water(-vapor)	Sulfate
free fixed Ammonia	Lime Salts
Tar	Hydrochloric Acid
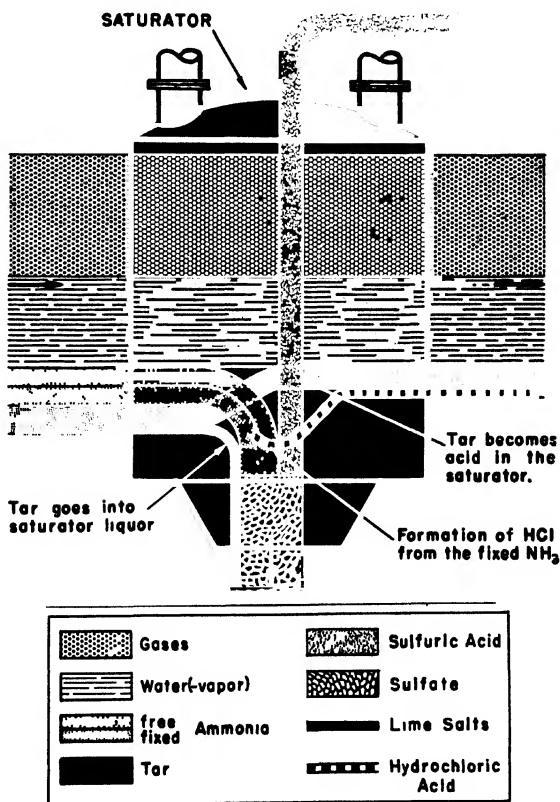
Fig. 3. "Direct" process for recovery of ammonium sulfate.[147]

mal dissociation of its salts. Descending the column of the still it finally meets a slurry of lime, which decomposes the fixed ammonia salts. The waste waters containing lime salts and impurities of the original liquor are discharged. The gases leaving the top of the still, which contain all the ammonia, pyridine bases, carbon dioxide, hydrogen sulfide, hydrogen cyanide, and steam, pass into a vessel in which they come in contact with sulfuric acid. This saturator is operated either intermittently or continuously. When the concentration of ammonium sulfate in the saturator liquor has reached such a point that solid salt is deposited, the crystal mush is spread on drain tables to allow the mother liquor to run off, and then is put into centrifuges, in which the salt is finally given a short water wash. Details of this rather antiquated indirect ammonia-recovery process, and a splendid survey of its development and of the various pieces of apparatus, are to be found in Lunge-Köhler[4] and other textbooks such as Gluud and Jacobson,[12] Parrish,[146] and Porter.[18] Figure 2 is a flow diagram, with the necessary plant equipment superimposed, taken from a paper by Ohnesorge.[147]

The rather complicated set-up of the indirect process, the high capital investment, the large space requirements, and the problem of disposing of large quantities of stillwaste led Brunck[118] to the thought of recovering ammonia from the gas stream directly by absorption in acid rather than in water as the intermediary. The idea was doubtless sound, but insurmountable practical difficulties prevented its adoption

except in a few isolated plants. In its original form the Brunck process contemplated passing the hot gases, ammonia, tar, and all through concentrated sulfuric acid. Of necessity tar separated out and was acted upon by the acid; in consequence, the tar was of inferior quality and had to be specially treated to remove the acid. Sometimes even the more sensitive compounds of the gas were attacked by the sulfuric acid. To make matters worse, the considerable quantities of ammonium chloride contained in the gas were decomposed in the saturator with the evolution of hydrogen chloride, which severely attacked the apparatus. Moreover, the ammonium sulfate was badly contaminated by tar and could not be sold. Brunck overcame the troubles encountered by the tar by developing an ingenious system of tar separation, but some of the other handicaps remained. Otto[149] tried to perfect the Brunck scheme and put many plants into operation, but few of them survived without modification. His major deviation from the Brunck process was the use of a tar-ammonia liquor spray to remove the tar from the hot gas. Even though many of the troubles of the Brunck process were overcome in this way, the aim of Brunck's original thought was defeated, since ammonia liquor was again produced, necessitating an ammonia still unless it was discarded with an attendant loss of ammonia. Though this liquor production is usually soft-pedaled, it is there, and the process therefore is no longer a true direct process. If the ammonia liquor was evaporated in the saturator, the same ammonium chloride troubles which had confronted Brunck were reintroduced. Schreiber[150] pointed out

146 Parrish, P., *Design and Working of Ammonia Stills,* Ernest Benn, London, 1924, 313 pp.

147 Ohnesorge, O., *Brennstoff-Chem.,* 4, 118 22 (1923).

148 Brunck, R., Brit. Pat. 8,287 (1903); Ger. Pats. 167,022 (1905), 181,384 (1907); U. S. Pat. 825,297 (1906).

149 Dr. C. Otto & Co. G.m.b.H., Ger. Pat. 203,-254 (1908).

150 Schreiber, F., *J. Gasbeleucht.,* 53, 244–6 (1910). Gluud, W., and Jacobson, D. L., p. 589 of ref. 12.

this danger of hydrogen chloride in the saturator and the following equipment, as did Parrish,[151] and Furth [152] found sulfate obtained by the Otto process to contain 1 20 percent of ammonium chloride

Berthelot [153] pointed out as a serious disadvantage of direct processes that the considerable amounts of ammonium chloride often entrained in the tar cause serious damage to tar-distilling equipment if not removed by a water wash   Figure 3 illustrates the direct process in Ohnesorge's [147] fashion   Hilgenstock [154] has given a simple account of it

151 Parrish P   *Gas J*, **183**, 677-9 (1928)   *Chem Age (London)* **19**, 280 2 (1928)   *Trans Fuel Conf World Power Conf London 1928* **2**, 450 66 (1929)

152 Fürth, A,   *J Gasbeleucht*, **54**, 1030-4 (1911)

153 Berthelot C   *Bull soc ind nord* **46**, 87-192 (1919)   *Chem Abs* **14**, 2075 (1920)

154 Hilgenstock G, *Stahl u Eisen*, **29**, 1644 8 (1909)

Koppers [155] struck a compromise between the two extremes, and the phenomenal success of his idea proves again the value of the golden mean   In his process, the gas coming from the collecting main is cooled, just as in the indirect process, to such a point that substantial quantities of water are separated, in this practically all the fixed ammonium salts and some free ammonia dissolve   There remains in the gas about 75 percent of the total ammonia   The small amount of ammonia liquor is treated in the same kind of still as in the indirect process, the ammonia evolved is united with the main gas stream, which has previously been freed of tar fog, the gas is reheated above its dew point, and then passes through sulfuric acid in a saturator   Figure 4 shows the Ohne-

155 Koppers H   U S Pats 846 035 862 976 (1907) Reissue 12 971 on 862 976 (1909), Ger Pat 181 840 (1907)

COOLER

TAR SEPARATOR

SUPERHEATER

SATURATOR

Separation of fixed NH₃ by condensed water

STILL

Transfer of water to the gas by evaporation, i e according to partial pressure at a temperature under 100°C

Formation of pure solid sulfate

Reunion of both portions of NH₃ (in free form)

Separation of tar from the gas

Separation of the tar from the gas liquor

Decomposition of fixed NH₃ with formation of lime salts

Removal of NH₃ by steam

Reduced amount of still waste

Fic 4   Semi direct process for recovery of ammonium sulfate [147]

sorge [147] diagram for the semi-direct process; Fig. 5 shows a typical ammonia still; and Fig. 6 represents a saturator. Koppers achieved notable results in his process: he eliminated the tar and ammonium chloride troubles of Brunck, he made worthwhile economies as to steam and water consumption in comparison with the indirect process, and he substantially alleviated the waste-liquor problem.

Crucial for both the direct and semi-direct processes is the maintenance of a proper water balance, since ammonium sulfate is to be recovered from the saturator in solid form. In the direct process particular care must be exercised, inasmuch as all the water contained in the gas must pass through the saturator without condensation. This means that tar separation must be carried out at a sufficiently high temperature to allow an ample heat gradient across the system. The high temperature in turn makes adequate tar separation very difficult, as was discovered by Brunck. Of course, the heat of reaction evolved when ammonia is neutralized with sulfuric acid is helpful, but Brunck was forced to resort to the use of concentrated sulfuric acid in order to keep extraneous water out of the system. This produced undesired effects on tar and gas and increased acid consumption.

In this respect the semi-direct process is much better. Since in it the gas is cooled considerably below its dew point, the gas is unsaturated with water after it leaves the reheater. Therefore the cheaper 60° Baumé acid can be used in the saturator, which actually functions as an evaporator. The low temperatures maintained in the primary coolers allow a much better tar separation than in the direct process, and the dilute acid used in the saturator, according to Schreiber, [150] does not affect the gas. Figures 7 and 8, which are taken from a paper by Ohnesorge [156] on the history of ammonia-recovery processes, illustrate the temperature gradients of the direct and semi-direct processes.

A most excellent study of theoretical considerations involved in the various ammonia-recovery processes was published by Still. [157] He calculated equilibrium conditions and heat balances, gave vapor tensions in the saturators at various temperatures, salt and acid concentrations, dew points, cooling temperatures, heats of reaction, heat losses of equipment, and other data. Still concluded that in both the direct and semi-direct processes the heat of reaction is sufficient to cover all the heat losses and even to vaporize some extraneous water.

Steam consumption, which is quite a talking point when comparing the three systems, was calculated for coke-oven and gasworks practice by Krieger. [158] He came to the conclusion that nothing is gained for gasworks by using the direct process, since the lower steam consumption is counterbalanced by greater power requirements. Krieger also pointed out the danger of getting ammonium chloride into the saturators and into the tar.

Many papers have appeared which compare the advantages and disadvantages of the direct, semi-direct, and indirect systems and give their future prospects. Those written while the development work was still going on are often contradictory, and even those published more recently do not always agree. One of the best is doubtless a paper by Ohnesorge, [147] which shows the cool thinking of the patent attorney,

[156] Ohnesorge, O., *Stahl u. Eisen*, **30**, 113–6 (1910).

[157] Still, C., *Glückauf*, **47**, 1509–17, 1549–57, 1600–8 (1911). Lunge-Köhler, Vol. 2, p. 161, of ref. 4.

[158] Krieger, A., *Gas- u. Wasserfach*, **65**, 17–20 (1921).
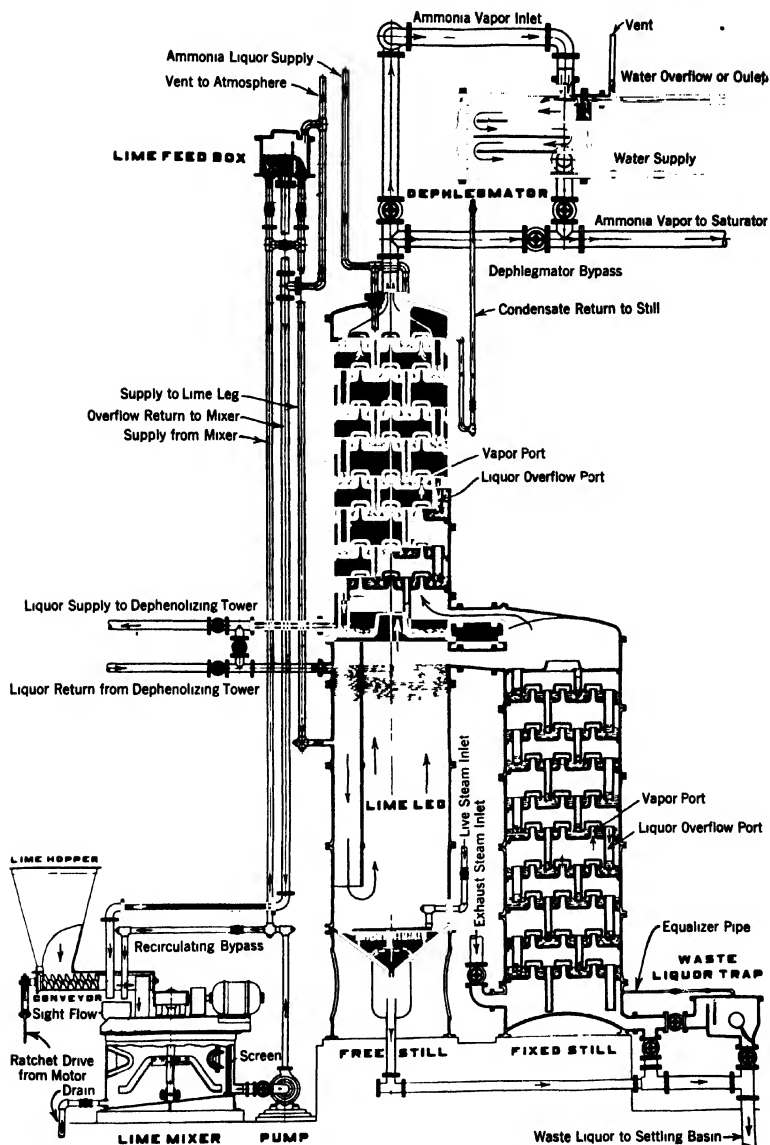
Fig. 5. Koppers ammonia still.
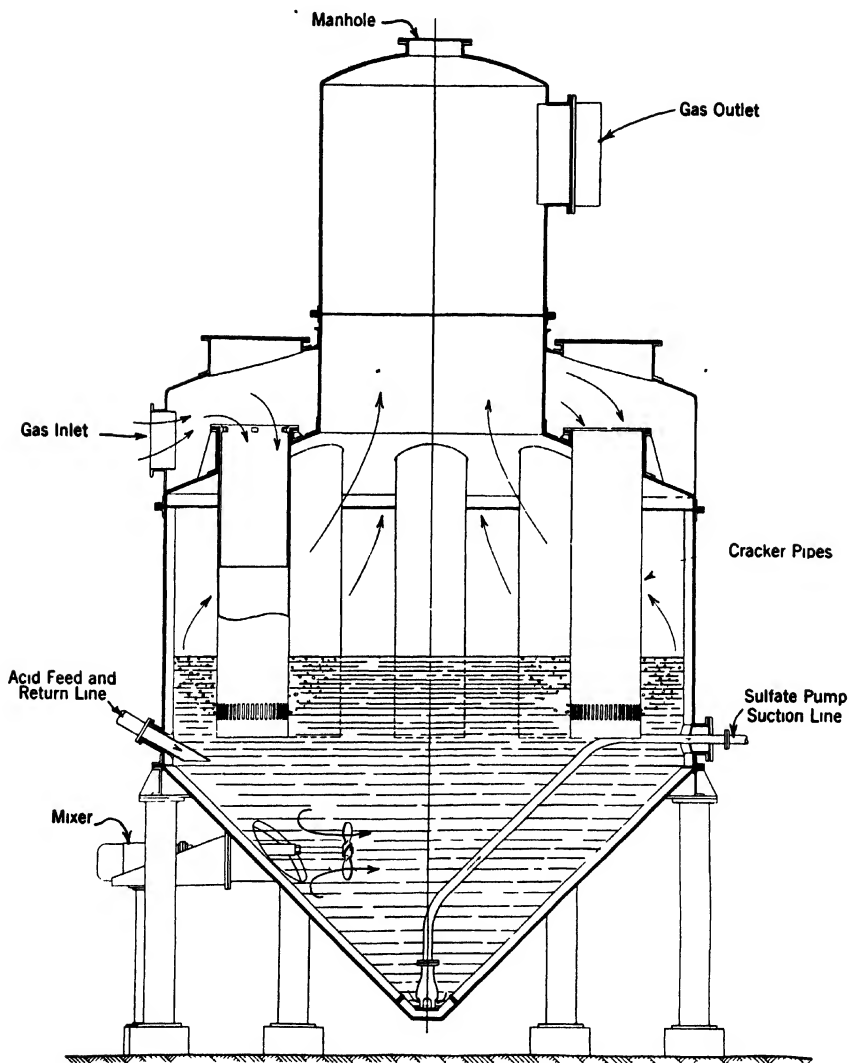
FIG. 6. Koppers ammonia saturator
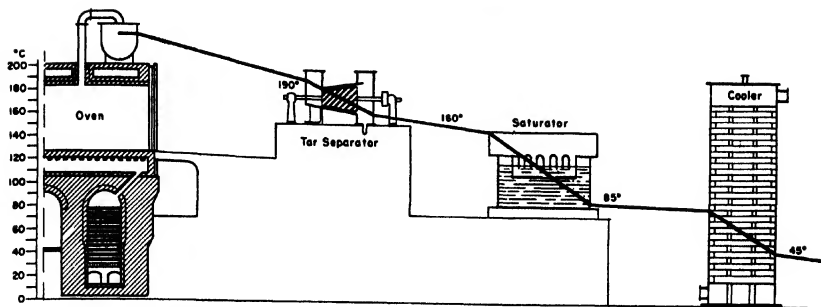
FIG. 7. Temperature gradients in the 'direct" process for recovery of ammonium sulfate [156]

free from the petty jealousies and prides of the workers in the field However, the others [88, 150, 152, 153, 156, 159, 160, 161, 162] are

159 Schreiber, F , Z angew Chem , **25**, 2289 96 (1912)

160 Bertelsmann, W , Chem Ind , **39**, 88–96 (1916).

161 Muhlert, F , Chem Fabrik , **9**, 273–81 (1936) , Chem Abs , **30**, 5760 (1936)

162 Grebel, M A Gas World, **54**, 652–3 (1911) Meyn, W , Oesterr Z Berg Huttenw , **69**, 15–20 (1911) , Chem Abs , **4**, 1508 (1911) Douglas, A , J Gas Lighting, **118**, 157 (1912) Ohnesorge, O , Z angew Chem , **26**, 593 6 (1913) Heck, C , Stahl u Eisen, **33**, 777–82, 817–22 (1913) ; Gluckauf, **49**, 443 8 481–6 (1913) Riley, T H , J Gas Lighting, **133**, 257–60 (1916) Curphey W S , Gas World, **69**, 19 21 (1918) , Gas J , **143**, 68–9 111 3, 161 (1918) Smith, T B , Gas World, **70**, Coking Sect No 1789, 12 4 (1919) Gas J , **144**, 661–2 (1918) Liese K J Gasbeleucht , **62**, 113 9 (1919) Nicklin, M E Gas World, **74**, Coking Sect , No 1907 15 9 (1921), Gas J ,

well worth studying and are broadly summarized herewith

The greatest single advantage claimed for the indirect process is its elasticity, since it allows the manufacture of any desired grade of ammonia liquor and ammonium salt This is of greatest importance in adapting to changed market conditions and in meeting national emergencies when abnormally large quantities of nitrates and nitric acid are required Second in impor-

153, 280–2 (1921) Iron & Coal Trades Rev , **102**, 160 (1921) Luther, A , Gluckauf, **59**, 314 9 (1923) Foxwell, G E , Gas J , **188**, 768–70 (1929) Parker A , Gas J , **188**, No 3471, Inst Gas Eng Suppl, 37 41 (1929) Holton, A L Gas Engi , **48**, 382–5 (1931) Hollings, H and Pexton, S Trans Inst Gas Engrs , **78**, 266–8 (1928-9), **79**, 254–67, 305–34 (1929-30) Editorial, Progressive Age, **27**, 522 (1909) , Chem Abs , **3**, 2748, 4749 (1909)
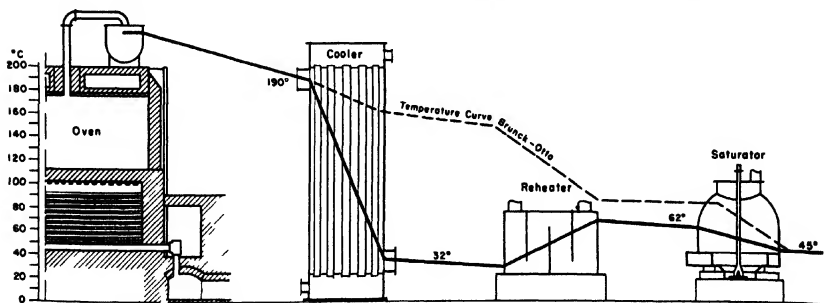
FIG 8 Temperature gradients in the "semi-direct" process for recovery of ammonium sulfate [156]

tance is the relative lack of interdependence of the various parts of the process: repairs are easily made without affecting the whole system. Finally, the tar removal is absolute.

On the debit side of the picture is the enormous volume of waste.liquors—more than double that of the semi-direct and sixteen times that of the direct system—the high steam consumption, high operating costs, large capital investment, large ground-space requirements, and the loss of ammonia at the scrubbers, from storage, and at the stills. Some of these items can be overcome in very large installations, particularly if a much stronger liquor can be produced. The prospects for the future of this process would appear to be better than in the past.

By its very nature the semi-direct process takes a stand in the middle. It has some elasticity, since products other than ammonium sulfate can be made to a limited extent from its smaller volume of ammonia liquor. The waste-liquor problem, though not eliminated, is materially reduced; capital and operating costs are lowered; less ground space is required; the steam consumption is lower; the ammonia recovery from the gas is higher by 5 percent (even 12 percent has been reported); it is almost as reliable as the indirect and more reliable than the direct process; the dilute acid in the saturator has no effect on the gas, in contrast to the direct process; and existing indirect installations can be changed over readily if desired. Its disadvantages are that it still has a waste-liquor problem, and that power costs may sometimes counterbalance the steam savings. The prospects for the future would seem to continue favorable, especially for plants of medium size.

The direct process has the smallest investment and operating cost of the three,

lowest ground-space requirements, lowest waste-liquor volume, lowest steam consumption, and ammonia recovery equal to the semi-direct and 5 percent higher than the indirect process.

Among the disadvantages stands out the problem of hydrogen chloride with its danger of destroying equipment and contaminating the sulfate. It is claimed that this trouble is largely overcome by proper control of the saturator temperature. Nevertheless, ammonium chloride often gets into the tar and must be removed if damage to tar-distilling equipment is to be avoided. As high as 3 to 5 percent of the fixed ammonium salts are said to get into the tar. The tar itself is of inferior quality, because the concentrated sulfuric acid in the saturator acts on it. Ammonium sulfate produced by the process is often contaminated by tar or colored red by thiocyanate. Operation is not foolproof, since unforeseen troubles often come up. Frequently steam heating must be used in the saturator to prevent dilution of the bath. The great saving of steam is often counterbalanced by increased power costs. Needless to say, the process has no flexibility and in that respect is the worst of them all.

As to its prospects, it may be said that they are practically nil. It was never used in America and was almost abandoned in Europe long ago, nor have changed conditions offered any factors conducive to its resuscitation.

Though the processes outlined above give a general pattern, innumerable modifications have, of course, been developed. They have been described in great detail in a number of textbooks,[4, 12] to which reference is made. Gluud and Jacobson,[12] in particular, also give profuse footnotes to existing patent and other literature. Two modern schemes are worthy of special mention since they bid fair to become of con-

siderable importance in the future. One of these is a modified indirect process designed to overcome two of the most serious disadvantages of the old process: high steam consumption and still-waste-disposal problem. It was described by Tramm[163] as follows. The gas from the collecting main is washed with a circulated, uncooled liquor. The temperature of the gas is lowered to 80 to 85° C, and all fixed ammonium salts are removed. Since the liquor is in equilibrium with the gas, it takes up very little free ammonia and dissociable ammonium salts. Thereafter the gas is scrubbed with water to remove the free ammonia, and the liquor is distilled in a regular ammonia still but without addition of lime, for which there is no need on account of the absence of fixed ammonium salts. As the still waste contains no lime salts, passing it through heat exchangers countercurrent to the incoming cold ammonia liquor saves steam for the still. The cold still waste is used again on the ammonia scrubbers or for cooling water. Thus there is no still-waste-disposal problem. The fixed ammonia liquor is circulated until it contains 3 to 4 percent ammonia, whereupon it is evaporated to yield a light gray salt of 28 percent ammonia content, consisting largely of ammonium chloride.

Another scheme is the cooling of the gases to low temperatures, usually from −10 to 0° C, whereby all the ammonia is removed as a strong aqueous liquor comprising an almost pure solution of ammonium carbonate of 20 to 30 percent strength. Cooling of the gas is carried out by absorption refrigeration, utilizing the sensible heat of the gases as they come from the ovens. Usually the crude gas right from the primary coolers is sprayed with ammonia liquor at −5 to 0° C, whereby it is itself reduced to about 0° C and is then washed with cold, pure water. In this manner tar, naphthalene, ammonia, and water are removed almost completely, the ammonia content of the final gas being about 8 grains per 1,000 cubic feet. This is close to the figure normally obtained after the saturator in the semi-direct process. A 12 percent liquor can be produced, but there are likely to be stoppages from solid ammonium bicarbonate, and the liquor concentration is therefore commonly kept at about 6 percent. Since a number of plants have been in successful operation for almost a decade, among them one producing 45,000,000 cubic feet of gas per day, the new process can be considered established. The advantages are obvious: the liquor volume is reduced below that of the semi-direct process so that one of the most important drawbacks of the indirect system is eliminated; tar is removed completely; steam consumption is lowered; and as an added advantage naphthalene and moisture are also taken out, with subsequent decreased corrosion of equipment and mains. The process, of course, retains the very desirable flexibility of the indirect process, of which it is in a sense a development For all these reasons, it seems destined to become a formidable competitor of the semi-direct process. The sponsors of the new scheme are Lenze and his coworker Rettenmaier. They and several other investigators have published their experiences, including plant diagrams and cost estimates, in a number of patents and papers.[164-6]

163 Tramm, H., *Stahl u. Eisen*, 48, 753–61 (1928).

164 Lenze, F., and Rettenmaier, A., *Gas- u. Wasserfach*, 69, 689–91 (1926).

165 Lenze, F., Ger. Pats. 457,264 (1928), 482,-880 (1929). Stoll, L., *Gas- u. Wasserfach*, 73, 1102–4 (1930). Lenze, F., and Rettenmaier, A., *ibid.*, 74, 1169–72 (1931); *Gas J.*, 197, 139–42 (1932). Stedling, F., *Gas- u. Wasserfach*, 75, 164–9 (1932). Muhlert, F., *Brennstoff-Chem.*,

Washing with water under pressure should, of course, produce the same result as cooling to low temperatures. This thought is embodied in several proposals which, however, never succeeded. But if in the future coke-oven gas should be fractionated for chemical utilization the pressure system should become of importance. Felt [167] proposed spraying gas under 150 pounds pressure or more with turkey-red oil, which is said to absorb water, ammonia, tar, and other impurities. According to Still,[168] gas, after tar removal, is compressed to 100 to 200 atmospheres pressure; water is injected, and the ammonia is recovered as a concentrated solution of ammonium bicarbonate and ammonium sulfide. The solution is collected in a tank, and solid salts separate on cooling. Mother liquors may be used again for injection into the compressed gas. The Linde Company [169] compresses the gas to 4 atmospheres at about 140° C, eliminates the naphthalene in liquid form by cooling from 105 to 50° C, injects dilute ammonia liquor into the gas stream, thus producing a 10 percent ammonia liquor, and removes the last traces of ammonia by a final pure water spray at 15° C.

AMMONIUM SULFATE

So much for the principal processes and more interesting proposals for the recovery of ammonia from gases. Whatever the treatment of the gases, eventually they are passed, in general practice, through an acid bath, the saturator, in which the ammonia is tied up to form a salt that can be re-covered and sold. The general construction of such a saturator has already been shown in Fig. 6, but it should be pointed out that this piece of apparatus has undergone many changes in the course of the development of the industry. Lunge-Köhler [4] is recommended for a study of its history, and Gluud and Jacobson [12] give an abundance of references to more recent developments. A good survey is also contained in two papers by Thau,[170, 171] a paper by Bertelsmann,[160] and some constructions and methods of operation since 1930 are disclosed by Schmalenbach, Hoesch-Köln Neuessen, Eissner, and Koppers.[172] The saturators are commonly constructed of steel with a covering of lead over the inside to prevent attack by the acid. Lead, however, is not wholly resistant, and the maintenance charges are therefore major items on the operating-cost balance sheets. Thau [173] suggested overcoming this handicap by using acid-proof tile or cement as a coating, with a thin sheet-lead layer underneath to guard against leaks through cracks.

Many of these newer saturator constructions doubtless were the outgrowth of the desire to improve the crystal size of the ammonium sulfate produced. In the heyday of the industry, the only object of the saturators was to get the ammonia out of the gas in some solid form that could be sold, and at that time the market was not very particular in its requirements as to

13, 350–2 (1932). Thyssen'sche Gas- und Wasserwerke, Ger. Pat. 583,417 (1933). Pippig, H., Gas- u. Wasserfach, 77, 346–9 (1934).

166 Wucherer, J., ibid., 78, 118–21 (1935).
167 Felt, W. O., U. S. Pat. 1,213,796 (1917).
168 Still, C., Brit. Pat. 147,787 (1920).
169 Gesellschaft für Linde's Eismaschinen A.-G., Brit. Pat. 281,288 (1926).

170 Thau, A., Gas- u. Wasserfach, 68, 799–805, 824–9 (1925).
171 Thau, A., Z. Ver. deut. Ing., Beiheft Folge 1937, No. 4, 105–11; Chem. Abs., 32, 313 (1938).
172 Schmalenbach, A., Fr. Pat. 699,553 (1930). Hoesch-Köln Neuessen A.-G. für Bergbau und Hüttenbetrieb, Fr. Pat. 717,883 (1931). Eissner, W., U. S. Pat. 1,880,925 (1932). Koppers, H., U.S. Pat. 2,141,186 (1938).
173 Thau, A., Glückauf, 55, 241–3 (1919); Gas- u. Wasserfach, 73, 767–75 (1930); Gas J., 191, 524 (1930).

size and shape. With the advent of the synthetic-ammonia industry the picture changed. The new producers were chemical manufacturers who had long ago learned to produce according to rigid specifications and were keen enough to attempt to capture the market with a product of superior qualities. Uniformity of crystal size and shape were especially stressed. The byproduct ammonia manufacturers simply had to follow suit, and their thought naturally turned to improving the apparatus. People who had been in the crystallizing business for many years were quite familiar with the doctrine that uniformity of crystals is not obtained by haphazardly throwing together the reacting materials, but only by keeping the crystallizing solution as close as possible to the "metastable zone" in which no new crystal nuclei are formed and the newly formed salt deposits on the nuclei already present. This ideal state cannot, of course, be attained in practice, but it can be approached by proper means, such as temperature and acid control, and especially by a definite motion of the bath. This motion brings small crystals back into the zone where fresh ammonia and acid are introduced, so that they grow to a desired size. These principles were embodied in many of the new designs.

For the same reasons, and for reasons of general plant efficiency, the actual operation of the saturator also came in for a great deal of attention. Lishmann [174] tried to find out why sulfates vary in appearance from plant to plant and even in the same plant from day to day. He favored keeping the concentration of the acid in the saturator below 5 to 6 percent and supervising the density of the bath. Thau [175]

gave an account of the best saturator operation, particularly with respect to preventing salt-crust formation, and Tupholme [176] stressed low acidity (1 to 1.5 percent) and a circulated bath. Hailstone [177] brought out the importance of maintaining the correct physical conditions within the saturator for a sufficient time to allow the crystals to grow, and of maintaining an unvarying low acidity. He also suggested refinements in saturator design. For control of the acidity he used a hydrometer, but recognizing its shortcomings suggested measuring the electrical conductivity of the liquor. Cranston and Stockdale [178] wanted to keep the liquor at 2 percent and carried out the suggestion of Hailstone by using a conductivity cell to regulate automatically the acid addition.

A great deal of work was also done on the physicochemical conditions prevailing in the saturator and generally in the system $(NH_4)_2SO_4$-H_2SO_4-H_2O. Lowe [179] made a study similar to that of Still,[157] referred to above, but confined to the saturator. He found that in the direct and semi-direct systems the heat of reaction is sufficient to evaporate all the mother liquor present and take care of heat losses. Challis and Hughes [180] found that at equilibrium a definite relationship exists between the density, temperature, and acid concentration of saturated solutions of ammonium sulfate in water and sulfuric acid, that ammonium sulfate is more soluble in sulfuric acid than in water, the solubility increas-

[174] Lishmann, G. P., *J. Soc. Chem. Ind.*, **31**, 269 (1912).

[175] Thau, A., *Glückauf*, **55**, 733–7 (1919).

[176] Tupholme, C. H. S., *Gas Age-Record*, **59**, 483, 486 (1927).

[177] Hailstone, H. J., *Gas J.*, **174**, 646–8 (1926).

[178] Cranston, J., and Stockdale, J., *J. Roy. Tech. Coll.* (*Glasgow*), **2**, No. 1, 36–9 (1929); *Chem. Abs.*, **23**, 4538 (1929).

[179] Lowe, H. M., *Gas World*, **81**, Coking Sect., 73–5 (1924).

[180] Challis, C. C., and Hughes, T. W., *J. Proc. Sydney Tech. Coll. Chem. Soc.*, **2**, 60–5 (1926); *Chem. Abs.*, **20**, 2728 (1926).

ing with temperature, and that the specific gravity of the mother liquor is a direct indication of the sulfuric acid concentration at the temperature of the saturator.

Terres and Schmidt [181] made solubility and vapor-pressure measurements on the ternary system NH_3-SO_3-H_2O (including both excess acid and ammonia) from 0 to 100° C, and they offered the corresponding diagrams. Crystals of ammonium sulfate separate on the ammoniacal side and on the acid side up to 20 to 22 percent by weight of free acid. At higher acid concentrations the double salt $NH_4HSO_4 \cdot (NH_4)_2SO_4$, and eventually NH_4HSO_4 alone, separate. From the vapor pressures, the acid concentration and the working temperature of the saturator may be determined. In the direct process the bath may contain 7 to 9 percent free acid and should be kept at 100° C or above if the gas used is saturated at 75 to 80° C. In the semi-direct process the temperature should be from 40 to 50° C. The thermal equilibrium in the saturator was discussed in detail in a paper by Terres and Patscheke [182] for the direct, semi-direct, and indirect processes, taking into account also the varying amounts of fixed and free ammonia in the gas. Salts such as ammonium bisulfide, ammonium cyanide, and ammonium carbamate are largely dissociated under the conditions of sulfate manufacture, so that the heat of reaction of the ammonia in coal gas with sulfuric acid is decreased only about 6 percent by their presence. A number of double salts of ammonium sulfate and sulfuric acid and their temperature range of existence have been described by Locuty and Laffitte [183] in thermal studies

in the system $(NH_4)_2SO_4$-H_2SO_4-H_2O. In a continuation of these studies Locuty [184] reported that pure ammonium sulfate as desired for fertilizer purposes will be deposited only if the sulfuric acid concentration does not exceed 19.5 percent at 90° C, 17.5 percent at 70° C, 15.2 percent at 50° C, 13.1 percent at 30° C, and 11.0 percent at 10° C.

In the early days of the industry little regard was shown for the ammonium sulfate itself. It was usually fished out of the saturator manually, with the aid of a ladle, and allowed to drain. From the drain board it was transferred to storage with whatever mother liquor adhered to it. Sometimes the warehouse was steam heated to aid in the drying of the salt, but usually nothing further was done with it. Later on centrifuges were added to the standard equipment; to these the drained salt was transferred for a more thorough elimination of the mother liquor. A short water wash in the centrifuge was employed in most plants to reduce the acidity to a minimum. A good account of the historic development of this phase of ammonia recovery is given by Lunge-Köhler.[4] Most of the plants in existence today have retained this combination of a continuous saturator (Fig. 6) and a batch centrifuge, such as is pictured in Fig. 9, but some have adopted a continuous scheme. This is the process of Wilton; as described in detail by an anonymous writer,[185] the centrifuge is replaced by a slow-moving, acid-proof, metal-cloth belt conveyor, which passes over suction boxes and thus separates the salt from the mother liquor. A later version of continuous ammonium sulfate recovery is pictured in Fig. 10.

As indicated above, the synthetic-ammo-

181 Terres, E., and Schmidt, W., *Gas- u. Wasserfach,* **70,** 725–8, 762–6, 784–6, 808–13 (1927).

182 Terres, E., and Patscheke, G., *ibid.,* **74,** 761–4, 792–9, 810–4, 837–41 (1931).

183 Locuty, P., and Laffitte, P., *Compt. rend.,* **199,** 950–2 (1934).

184 Locuty, P., *Rev. ind. minérale,* No. **348,** 275–97 (1935).

185 Anon., *J. usines gaz,* **52,** 271–3 (1928).

FIG. 9. Batch centrifuge.

Fig. 10. Baker Perkins continuous ammonium sulfate centrifuge. The raw slurry enters a rotating, sloping, horizontal inlet funnel (1) at its small end where the peripheral speed is relatively low. As the slurry passes down the inner face of the funnel it is gradually accelerated until it reaches the back of the perforated drum (2), where it moves at drum speed. The funnel is carried by equally spaced lugs attached to the pusher (3) which rotates with the drum and has a short reciprocating motion imparted to it by a piston rod (4) actuated by a hydraulic servo motor (5) which is a part of the main shaft (6). When the slurry is deposited on the slotted screen which lines the drum (2), the liquor is spun out into the first section of the wet housing (7). As the pusher (3) moves forward it forces the cake (8) across the face of the drum (2). On the return stroke of the pusher (3), space is left for more inflowing slurry to be deposited on the drum (2). The cake (8), equal in thickness to the difference in diameter of the outer edge of the funnel (1) and the slotted screen lining the drum (2), is gradually pushed across the screen. It passes under a wash spray (9), if washing is desired, and the wash liquor is spun out into the second section of the wet housing (11). Both sections of the wet housing (7) and (11) are equipped with liquor outlets so that mother liquor and wash liquor may be kept separate. When the cake (8) reaches the outer edge of the drum (2) it flies off into the dry salt collector housing (10).

nia industry brought about such a change in the buying habits of the public that a number of shortcomings of the old byproduct ammonium sulfate, which had always been known but had been neglected, were remedied in an effort to compete with the synthetic product on a parity basis. Some of these faults were real, such as moisture content, acidity, caking on storage, with resultant lack of free flow; others were immaterial as far as the usefulness of the salt was concerned—for example, color, odor, and content of incidental impurities.

The public generally buys by appearance, and since whiteness is almost synonymous with purity a gray or brown byproduct sulfate was immediately stamped as an inferior grade, even though its ammonia analysis might have been just as high as that of the synthetic product. Thau [170] called attention to these facts in a lengthy paper.

The oldest and probably most serious complaint concerned the notorious caking of byproduct ammonium sulfate. It was variously attributed to moisture, sulfuric acid, pyridine sulfate, and improper crys-

tal size, and the investigators did not quite agree on the cause of the trouble. Moisture doubtless received the first and the primary blame, and its elimination was striven for. Early efforts to provide means of drying centered on the installation of steam pipes in the warehouses. Then attempts were made to dry the salt more rationally, as by Müller's proposal [186] to blow dry air through the centrifuge after the water wash. Mechanical means such as rotary and tray driers were adopted a little later, and descriptions of such equipment are given by Gluud,[12] Thau,[170] and the South Metropolitan Gas Company.[187] However, the value of drying alone has been questioned from the beginning. After all, it means just a concentration of the sulfuric acid on the crystals, which will pick up moisture again at the first opportunity. There can be no question that the presence of free sulfuric acid in sulfate will promote caking. Sheard [188] found that sulfate retains moisture just about in proportion to its acid content. Oka [189] showed that pure sulfate is not hygroscopic, but that it becomes increasingly so with increasing free acid content. Burgevin [190] in a very fine study of the problem determined the hygroscopicity threshold values of samples of commercial ammonium sulfate. The threshold value is defined as the relative humidity, at a given temperature, above which the salt begins to absorb moisture and below which it begins to lose moisture. He found that, whereas pure salt had a

value of 80, that of commercial salts containing acid went down to 68 for the worst sample. Neutralization brought all values nearly up to that of pure salt, showing that the impurities other than sulfuric acid present in the commercial products have little or no effect on the hygroscopicity threshold. Drying commercial sulfate at 105° C has, according to Burgevin, practically no effect on its threshold. Greenfield [191] also discussed the caking of sulfate, listing free acid as one of the contributory causes.

The pyridine sulfate content of commercial ammonium sulfate is often cited as a cause of caking, for example by Atwater and Schultze [192] and by Macleod, Chapman, and Wilson.[193] The latter authors probably found the true explanation when they suggested that, on drying, pyridine might be split off, leaving free sulfuric acid on the crystal faces. This is very plausible, since pyridine sulfate is known to dissociate readily and to be stable only in the presence of excess sulfuric acid. All authors writing on pyridine sulfate agree that neutralization with ammonia eliminates the pyridine and the caking.

Another cause of sulfate caking is said to be improper crystal size and shape. Greenfield [191] considered a salt containing large and fine crystals to be particularly bad; Adam [194] agreed, finding that the higher the percentage of voids the less the tendency of sulfate to cake. All this makes good sense. It stands to reason that if with increasing humidity water is picked up by the salt, forming a strong solution

186 Müller, R., Ger. Pat. 223,098 (1908).

187 South Metropolitan Gas Co., Evans, E. V., and Hollings, H., Brit. Pat. 141,798 (1919). South Metropolitan Gas Co., Brit. Pat. 156,963 (1910).

188 Sheard, J. T., Gas World, 72, 542–3 (1920) ; Chem. Age (London), 2, 626–7 (1920).

189 Oka, S., J. Soc. Chem. Ind. Japan, 35, Suppl. binding 385–6 (1932) ; Chem. Abs., 26, 5389 (1932).

190 Burgevin, H., Chimie & industrie, Special No., 884–8, March, 1932.

191 Greenfield, G. J., Gas World, 84, Coking Sect., 28–9 (1926).

192 Atwater, C. G., and Schultze, J. F. W., Chem. & Met. Eng., 22, 373–4 (1920).

193 Macleod, J., Chapman, C., and Wilson, T. A., Gas J., 178, 291–4 (1927).

194 Adam, W. G., Chem. Trade J., 82, 3–4 (1928) ; Chem. Age (London), 18, 4–5 (1928) ; Gas World, 88, 4–5 (1928) ; Gas J., 181, 33–4 (1928).

of ammonium sulfate in sulfuric acid plus water, then with decreasing humidity the salt must precipitate out again, cementing the crystals together. If the voids are filled up with fines this cementing is going to be far worse than if large void space were available. As a further conclusion it follows of necessity that certain crystal forms, which break easily in handling and transit, must be less desirable than others. That this conclusion is really correct will be shown later.

Not only is the free sulfuric acid in by-product ammonium sulfate responsible for caking, but it is also the cause of the rapid destruction of iron equipment, bags, and other shipping containers. Therefore attempts to make neutral salt were appropriate. Many writers have contended that a proper saturator operation will go far toward this goal. Thau,[170] for instance, called attention to the fact that high acidity in the saturator causes small grains and packing of salt, with subsequent poor removal of mother liquor, and he fixed 5 percent acidity as the upper limit. Hailstone [195] also wanted better control in the saturator and use of a weak bath to insure production of large crystals. Evans [196] proposed to use a dilute bath at a high temperature so that no salt is formed in the saturator, to allow the bath to become alkaline, to discharge it, and to allow it to crystallize outside the saturator. Koppers [197] probably was the first to propose neutralization with ammonia. He wanted to keep one section of the saturator acid, the other ammoniacal. Hansford [198] used two saturators alternately, one alkaline and

one acid; Anon. [199] went back to the old Koppers proposal and used a two-compartment saturator and the same principle. The danger involved in any procedure in which alkaline conditions prevail in the saturator is the formation of blue salt. Hansford recognized this, but contended that his arrangement of apparatus and procedure precluded the trouble. Stavorinus,[200] however, was of the opinion that discoloration must always be faced if salt is made under alkaline conditions.

Far more work was done on the neutralization of acid sulfate produced in normal manner. Gardiner [201] tried to find out whether the acid was held within the crystals or merely adhered to the surface. Drainage and water-washing tests proved that the acid adhered to the surface and could be almost completely eliminated by proper draining and washing with neutral water. Capron [202] therefore treated sulfate in the centrifuge with a concentrated, neutral solution of ammonium sulfate, neutralized the acidulated solution thus formed with ammonia or ammonium carbonate, and recycled. Smart [203] believed that washing with a simple hot-water spray was effective.

It is only one step further to substitute ammonia liquor for water in the centrifuge, either instead of the customary water wash or after it. Wendriner [204] improved upon Capron's method by using a saturated sulfate solution containing free ammonia for the wash, and so did Wilton. Evans, Parrish and Valon, and Bateman used an ammonia solution as a wash in the centri-

[195] Hailstone, H. J., *Gas J.*, **166**, 102–4 (1924).

[196] Evans, E. V., and South Metropolitan Gas Co., Brit. Pat. 111,309 (1916).

[197] Koppers, H., Brit. Pat. 834 (1913).

[198] Hansford, J. B., *Gas World*, **75**, 243–4 (1921) ; *Gas J.*, **155**, 721–3 (1921).

[199] Anon., *Iron & Coal Trades Rev.*, **106**, 528 (1923).

[200] Stavorinus, D., *Gas- u. Wasserfach*, **68**, 776–8 (1925).

[201] Gardiner, P. C., *Gas J.*, **145**, 65 (1919).

[202] Capron, F., Brit. Pat. 108,990 (1916) ; U. S. Pat. 1,266,212 (1918).

[203] Smart, P. F., *Gas World*, **80**, 358–9 (1924).

[204] Wendriner, M., Ger. Pat. 247,808 (1910).

fuge.[205, 206, 207] Since impure liquor causes discoloration, the solution is usually made from the vapors of the fixed ammonia still or by distilling sulfate with lime. The Wilton process [185] made use of such neutralization to perfect continuous sulfate production. Before the endless belt reached the suction boxes, dilute ammonia liquor was sprinkled on the salt, so that neutral sulfate was produced. It was delivered by the belt to a drier consisting of a bundle of steam-heated tubes.

The use of ammonia gas for the neutralization of free acid was proposed with remarkable foresight by Koppers [208] at a time when the industry was still in its infancy and when nobody thought that it would ever become a pressing need. His suggestion was taken up by Adam,[209] who worked out mechanical details, and by Schramm,[210] Buckley,[211] and Dodd.[211]

If ammonia liquor is used in the centrifuge serious troubles may result: the copper of the centrifuge baskets corrodes severely; salt crusts may form in the saturator because of local alkalinity where the wash liquors are introduced; [207] and the workmen are bothered by liberated pyridine.[206]

Solid neutralizing agents also came in for due consideration. Linder [212] in an early patent claimed the use of solid ammonium carbonate, and Bateman [207] considered it the best of all materials ever proposed for the purpose. Linder and others [213] advocated solid fixed alkalies, alkaline earths, and magnesium in the form of their oxides, hydroxides, and carbonates, but Johnson [214] and Bateman,[207] who tried them out, found nothing to recommend them. On the other hand, Thau [170] had a good word to say for some of them. It would seem that these materials are undesirable because they leave residues in the sulfate which will show up in a lowered ammonia analysis. Linder and Weight [215] proposed the use of ammonium sulfite or bisulfite. In view of the corrosive nature of the sulfur dioxide evolved this would hardly be called practical. A very sensible suggestion was made at an early date by England,[216] who wanted to add finely ground phosphates to bind the free sulfuric acid and moisture. Strangely enough, this suggestion was never taken up and worked out.

Reviews of the whole art of neutralizing commercial ammonium sulfate are given by Thau,[170] Stavorinus,[200] Parrish,[217] Heigham,[217] and Weindel.[218] Their study is recommended to those seeking the practical man's viewpoint.

The second great handicap of byproduct ammonium sulfate is its color. Though it is perfectly true that natives in faraway lands occasionally refused to take white

205 Wilton, N., Brit. Pat. 127,398 (1918). Parrish, P., and Valon, W., U. S. Pat. 1,360,785 (1920). Bateman, C., Gas J., 166, 750–2 (1924).

206 Evans, E. V., ibid., 152, 515–20 (1920); Chem. Age (London), 3, 588–9 (1920); Gas World, 73, 422–6 (1920).

207 Bateman, C., ibid., 84, 280–3 (1926).

208 Koppers, H., Ger. Pat. 254,014 (1911).

209 Adam, W. G., Brit. Pat. 108,098 (1916).

210 Schramm, E., Brennstoff-Chem., 9, 46–7 (1928).

211 Buckley, W. E., Gas World, 95, No. 2448, Coking Sect., 83–4 (1931). Dodd, A., ibid., 108, No. 2809, Coking Sect., 63–72 (1938).

212 Linder, S. E., Brit. Pat. 121,082 (1918).

213 Linder, S. E., Brit. Pat. 127,715 (1918). Linder, S. E., and Lessing, R., Brit. Pat. 141,787 (1919); U. S. Pat. 1,377,493 (1921). Harvey, E. W., U. S. Pat. 1,608,737 (1926).

214 Johnson, T., Gas J. 157, 576–7 (1922); Gas World, 76, No. 1963, Coking Sect., 14–8 (1922).

215 Linder, S. E., Brit. Pat. 127,716 (1918); South Metropolitan Gas Co. and Weight, O. W., Brit. Pat. 141,799 (1919).

216 England, R., Brit. Pat. 10,781 (1908).

217 Parrish, P., Gas World, 76, 73–4 (1922); Chem. Age (London), 6, 97–8 (1922). Heigham, P., ibid., 10, 669–70 (1924).

218 Weindel, A., Brennstoff-Chem., 8, 104–7 (1927).

synthetic sulfate because they were accustomed to the gray-brown coke-oven salt, in general and for the bulk of the market, a clean, white salt will always have the better sales appeal. Discolorations most frequently experienced are gray, brown, yellow, blue, and red.[219] They may have a variety of causes. Tar and similar organic impurities are almost always present, often in lumps of substantial size, giving the salt a gray or brownish color; their removal would best be accomplished by filtration of the saturator bath before crystallization, as was proposed by Singer[220] and by Weindel,[218] or by skimming the bath, which would not be feasible in modern operation. Lessing[221] advocated a mechanical separation of solid impurities from solid sulfate by an elutriation process in which the impure salt is suspended in agitated concentrated sulfate solution and the impurities are floated off.

Most of the color, however, is due to inorganic constituents, chiefly sulfides. Van den Bossche[222] mentioned in particular iron sulfide; Leo[223] thought a gray color is mostly due to lead and copper, the copper having an especially strong coloring power; he ascribed a yellow color to arsenic or cadmium. An anonymous paper[224] also made arsenic sulfide responsible for a yellow color, though iron sulfates were suggested as a further cause. Thau[170] believed that gray and black were due to iron sulfide formed in neutral zones in the saturator, and Schramm[210] contended that metal carbonates and sulfides were formed

by corrosion of the pipes leading to the saturator. Weindel[218] cited the sulfides of iron, lead, copper, and arsenic, and traced them to the sulfuric acid used and to the metal parts of the saturator and centrifuge. He also pointed out that neutralization with impure ammonia liquor is often to blame for bad contamination with iron sulfide, and that use of ammonia in the centrifuge puts copper salts into the saturator. These dangers have already been mentioned. Small quantities of a large number of elements are present in commercial sulfate but probably do not contribute materially to discoloration. Ballard[225] found by spectroscopic examination of American byproduct ammonium sulfate: calcium, magnesium, iron, copper, zinc, aluminum, silicon, sodium, and lead. Only four of these could possibly give color.

Blue coloration of sulfate is doubtless due to complex iron cyanides. Although this trouble is far less frequent at modern semidirect plants than at the older indirect ones, it has received more consideration than any of the other discolorations. Bailey[226] at an early date called attention to it and thought that low temperatures rather than alkalinity were to blame. Thau[227] wrote a paper on the same subject at about the same time, discussing the causes of the formation of Prussian blue and describing methods to prevent it. He took the subject up in a number of later publications[170, 173, 175, 228] and finally came to the conclusion that blue iron complexes are primarily formed in the ammonia stillhead and the piping to the saturator, but only when there is insufficient steam and

219 Anon., *Gas World*, **62**, Coking Sect., 18–9 (1915).

220 Singer, L., Brit. Pat. 109,269 (1917).

221 Lessing, R., Brit. Pat. 152,766 (1919).

222 Van den Bossche, J., *Chimiste*, **5**, 17–8 (1914); *Chem. Abs.*, **8**, 3282 (1914).

223 Leo, K., *Gas World*, **60**, 620 (1914); *J. Gas Lighting*, **125**, 831–3 (1914).

224 Anon., *Chem. Age* (London), **3**, 678–80 (1920).

225 Ballard, S. S., *Hawaiian Planters' Record*, **42**, 185–95 (1938); *Chem. Abs.*, **33**, 300 (1939).

226 Bailey, H. J., *J. Soc. Chem. Ind.*, **26**, 377 (1907).

227 Thau, A., *Glückauf*, **43**, 95–7 (1908).

228 Thau, A., *Gas World*, **71**, No. 1833, Coking Sect., 11 (1919).

too low temperatures, which lead to condensation of water on the iron equipment, with subsequent formation of iron sulfide and through that of Prussian blue. Other papers dealing with blue discoloration are those of Schramm,[210] van den Bossche,[222] Leo,[223] and Anon.[224] They all agreed that cyanogen is the cause.

A red color is sometimes seen in byproduct sulfate, which may be due to the presence of thiocyanate. Lloyd[229] found thiocyanates in commercial salts, Thau[170] and Leo[223] made ferric thiocyanate responsible for the color, and Anon.[224] attributed it to ferric thiocyanate or phenols.

In concluding this résumé it should be pointed out that the elimination of sulfate discoloration is something to strive for not only on account of the greater popular appeal of a white salt but also because some of the impurities may be definitely harmful to the bacterial life of the soil to which the sulfate is added as a fertilizer. Lloyd[229] emphasized this very strongly.

More modern considerations of ammonium sulfate have dealt to an astounding extent with the size and shape of its crystals. We have already indicated that agitation, acid and ammonia concentration, temperature, and saturator construction play an important role in determining the size of crystals obtained. But size is not everything. Obviously a long, needle-shaped crystal would tend to break in handling and in transit, with resultant production of fines and filling of the voids with small pieces and powder. This would make the salt liable to caking with changing humidity of the atmosphere. Short, chubby crystals, on the other hand, are mechanically much stronger and would preserve almost indefinitely the large void

spaces among them. Both sorts of crystals may belong to the same crystal class, differing merely in their habit. It is well known that the habit with which a crystal may form is often profoundly influenced by small amounts of other compounds present in the solution during crystallization. Such compounds are usually referred to as solution associates. This field of solution associates and their influence on the crystal habitus and size has been made the subject of intense study. Much of this work has been carried out by the producers of synthetic ammonia, and coke-oven men should be able to take advantage of it in the improvement of their own product. Though most of the results are contained in patents, some very worthwhile papers have also been published.

The Société de fours à coke et d'entreprises industrielles[230] removed copper and arsenic from the bath and reduced ferric to ferrous salts; the Société de mines de Dourges[231] reduced ferric to ferrous salts with the aid of hydrogen sulfide. Seidler[232] added to the crystallizing solution such materials as wood extract (waste sulfite liquor) or other vegetable extracts such as pectin or hydropectin. Adam and Murdoch[233] prepared ammonium sulfate of elongated crystal structure by adding to the bath salts of trivalent iron, or of chromium, aluminum, titanium, beryllium, zirconium, thorium, or yttrium, chromates or dichromates.

Von Kreisler[234] found that coarse crys-

[229] Lloyd, F. J., *Chem. News*, **98**, 172–3 (1909); *Engrais*, **23**, 1177 (1909); *Chem. Abs.*, **3**, 1820 (1909).

[230] Société de fours à coke et d'entreprises industrielles, Fr. Pat. 637,977 (1926).
[231] Société de mines de Dourges, Fr. Pat. 637,-997 (1927).
[232] Chemische Fabrik Gross-Weissandt G.m.b.H. and Seidler, P., Ger. Pat. 519,517 (1927).
[233] Adam, W. G., Fr. Pat. 697,657 (1930). Adam, W. G., Murdoch, D. G., and Gas Light and Coke Co., Brit. Pat. 330,945 (1929); U. S. Pat. 1,919,707 (1933).
[234] Von Kreisler, A., Fr. Pat. 760,029 (1934); U. S. Pat. 2,021,098 (1936).

tals are produced by addition of urea. He used 2 to 6 parts per 100 parts sulfate, and the final product may contain from 0.1 to 0.5 percent urea. Gluud, Klempt, and Ritter [235] found iron most harmful in a saturator, and they devised methods and apparatus for its removal. In the preferred arrangement salt was made until the mother liquor contained too much iron. Then the bath was allowed to become ammoniacal, whereby the iron was precipitated as sulfide and was removed. It might also be removed after proper oxidation as ferric hydroxide. The iron was removed in a similar manner by Tielken and Riese,[236] and by Deutsche Ammoniak-Verkaufs-Vereinigung.[237] The I. G. Farbenindustrie [238] proposed the addition of aluminum salts to the bath. Aluminum sulfate might be added to the extent of 0.003 to 0.7 per 1,000 (calculated as Al_2O_3). As auxiliary agents there might be used salts of sodium, potassium, zinc, and manganese. In a similar group of patents to the I. G. Farbenindustrie [239] there was also added an aluminum salt, but besides that there were mentioned various combinations with manganese, zinc, sodium, potassium, magnesium, iron, and organic sulfonic acids (such as phenolsulfonic acid). In a third group of patents to the I. G. Farbenindustrie [240] aluminum was replaced by chromium and trivalent iron, in combination with sodium, manganese, zinc, magnesium, and organic sulfonic acids (such as aniline disulfonic acid). The chromium and iron might be in the form of complex salts such as ferro- and ferricyanides. Rayner and the Imperial Chemical Industries [241] removed trivalent ions, such as those of iron, aluminum, or chromium, by the addition of enough oxalate of ammonium, sodium, or calcium to precipitate them. The same object of removing iron, aluminum, or chromium ions was achieved by Applebey and Imperial Chemical Industries [242] by the addition of hydrofluoric, hydrocyanic, or thiocyanic acids or their salts, which bind the metal ions in complex form. As auxiliary substances there might be used glucose, cane sugar, black treacle, and molasses. Berkhoff and the Staatsmijnen in Limburg [243] removed iron, aluminum, and chromium from saturator baths by the addition of phosphoric acid or acid-soluble phosphates, and in another patent [244] they substituted arsenates for the phosphates.

Gluud, Klempt, and Ritter [245] made an extensive study of the effects of various conditions upon the crystal form of byproduct ammonium sulfate. Impurities such as pyridine, tar acids, and arsenic ap-

[235] Gluud, W., Klempt, W., and Ritter, H., Ger. Pat. 563,552 (1930). Klempt, W., Ger. Pat. 631,353 (1936). Ges. für Kohlentechnik m.b.H., Fr. Pat. 762,636 (1934).

[236] Tielken, O., and Riese, W., Ger. Pat. 598,-773 (1934).

[237] Deutsche Ammoniak-Verkaufs-Vereinigung, G.m.b.H., Ger. Pat. 632,181 (1936).

[238] I. G. Farbenindustrie A.-G., Fr. Pats. 781,-750, 789,995 (1935). Jeltsch, A., and Strzyzewski, A., U. S. Pat. 2,092,073 (1937).

[239] Rumscheidt, C., Jeltsch, A., Strzyzewski, A., and Hegge, H., U. S. Pat. 2,043,066 (1936); Ger. Pats. 648,539, 651,311 (1937).

[240] I. G. Farbenindustrie A.-G., Fr. Pat. 786,-321 (1935); Brit. Pat. 440,807 (1936). Rum-

scheidt, C., and Strzyzewski, A., U. S. Pat. 2,099,079 (1937).

[241] Rayner, J. W. R., and Imperial Chemical Industries Ltd., Brit. Pat. 484,921 (1938). Imperial Chemical Industries of Australia and New Zealand Ltd., Australian Pat. 104,689 (1938).

[242] Applebey, M. P., and Imperial Chemical Industries Ltd., Brit. Pat. 485,164 (1938). Imperial Chemical Industries of Australia and New Zealand Ltd., Australian Pat. 104,688 (1938).

[243] Berkhoff, G., Jr., Fr. Pat. 767,290 (1920); U. S. Pat. 2,102,107 (1937). De Directie van de Staatsmijnen in Limburg, Dutch Pat. 39,571 (1936).

[244] De Directie van de Staatsmijnen in Limburg, Fr. Pat. 838,977 (1939).

[245] Gluud, W., Klempt, W., and Ritter, H., Ber. Ges. Kohlentech., 3, 371–84 (1931).

peared to have no effect, and iron in its trivalent form was found to be the determining factor. Chromium and aluminum were equally detrimental. On the other hand, the lower-valence forms of iron, manganese, and cobalt exerted a very favorable influence. The authors proposed to eliminate the deleterious iron compounds by oxidation and precipitation as hydroxide. A paper by Klempt [246] expanded the previous one in several directions.

Berkhoff [247] also investigated the shape and size of ammonium sulfate crystals as they are influenced by physical and chemical means and came to conclusions which essentially agree with those of Gluud and his coworkers. He suggested the removal of iron (aluminum, chromium) by the addition of superphosphate in an amount of 44 pounds of 14 percent superphosphate to a saturator of 460 cubic feet capacity and from 0.5 to 1.0 percent acidity. Among desirable physical conditions he mentioned homogeneity of the bath produced by proper agitation, constant acidity, constant total crystal-surface area, and prevention of local nucleus formation. Eissner [248] discussed the influence of various compounds on the crystal habit of ammonium sulfate and illustrated his points with diagrams and photomicrographs. Perel'man and Strakhova [249] advocated an acidity of not over 1 to 2 percent and the elimination of trivalent ions by superphosphate or ground phosphate rock. There seems nothing in their paper to distinguish their work from that of Gluud et al. and of Berkhoff. Fi-

nally, Travers [250] described the detrimental effect of trivalent iron and suggested reduction to the innocuous divalent form. A general review of methods and apparatus for the production of coarse-grained ammonium sulfate has been given by Thau.[251]

Although sulfuric acid is practically the only agent used to bind ammonia contained in distillation gases, a number of other acids and acidic materials have been employed. Foremost, perhaps, is niter cake, sodium acid sulfate, which gained some prominence during and after the first world war. At that time sulfuric acid became quite scarce, owing to the needs of the war industries, and efforts were made to utilize the one-half of the acid still contained in the residue from nitric acid manufacture.

The use of this material had already been suggested at the end of the last century by Price [252] but was forgotten until the English government recommended it as an economy measure during the first world war. Cooper [253] reprinted the government's advice and gave some of his own observations. A solution of equal parts by weight of water and niter cake is mixed with sulfuric acid in the ratio of 2 to 3 and heated to about 200° F. The acidity in the saturator is maintained at about 6 percent. Sodium sulfate is obtained in the beginning, but ammonium sulfate is soon recovered in a purity of about 83 percent. The process saves from 15 to 25 percent sulfuric acid, but the sodium sulfate content and a rather high acidity of the product are undesirable features. The British Sulphate of Ammonia

246 Klempt, W., *ibid.*, **4**, 191–202 (1933).

247 Berkhoff, G., Jr., *Chem. Weekblad*, **32**, 186–97 (1935) ; *Chem. App.*, **23**, 104–7, 118–9, 125–7 (1936).

248 Eissner, W., *Fortschr. landw.-chem. Forsch.*, **1937**, 208–17 ; *Chem. Abs.*, **33**, 3957 (1939).

249 Perel'man, S., and Strakhova, E., *J. Chem. Ind. (U.S.S.R.)*, **15**, No. 7, 26–31 (1938) ; *Chem. Abs.*, **32**, 8840 (1938).

250 Travers, A., *Congr. chim. ind., Compt. rend. 18me Congr.*, Nancy, Sept.-Oct., **1938**, 82–3 ; *Chem. Abs.*, **33**, 6533 (1939).

251 Thau, A., *Coal Carbonisation*, **3**, 173–5 (1937). **4**, 27–8 (1938).

252 Price, A. P., Brit. Pat. 6,983 (1884).

253 Cooper, G. S., *Chem. Trade J.*, **58**, 235 (1916) ; *J. Gas Lighting*, **133**, 523–4 (1916).

Association, in a publication [254] by an anonymous author, took cognizance of the situation and advised that (1) the process should be used only during the war; (2) no salt of less than 24 percent ammonia should be made; (3) the niter cake used should not contain more than 0.05 percent nitric acid, in order to avoid damage to the lead lining of the saturator; (4) not more than 10 percent sodium bisulfate should be used. Gavin [255] reported on practical tests in which a salt with 23.59 percent ammonia, 0.78 percent free acid, and 3 percent moisture was produced. The Société industrielle de produits chimiques [256] treated an aqueous solution of niter cake with excess ammonia and precipitated the sodium as bicarbonate with carbon dioxide. According to other patents of the same company [257] a double salt ($NaNH_4SO_4$) is made from niter cake. A solution of this salt at 111° C precipitates sodium sulfate and allows the recovery of ammonium sulfate at 70° C. In modifications of this process the separation of the sodium sulfate is carried out at 0° C, or the double salt is heated to 350–600° C, thereby expelling ammonia and reforming sodium bisulfate. A later patent to the same company [258] expanded this last idea of recovering ammonia by heating the double salt. Fischer and Niggemann [259] found the process quite feasible technically but thought it best to aim at the double

salt as a final product. Dawson [260] in a patent and in excellent phase-equilibrium studies gave abundant data on how best to carry out the process. Fertilizer tests proved that the sodium sulfate contained as an impurity in the ammonium sulfate is an accessory fertilizer and raised the yield per acre considerably. An anonymous paper [261] pointed out that up to 10 percent sodium sulfate content does no harm when the ammonium sulfate is used as a fertilizer; on the contrary, it aids in the assimilation of potassium from the soil. The paper also advised dissolving the niter cake used in the process in sulfuric acid and not in water, in order to avoid dilution in the saturator. The nitrate limit was set at "less than 0.25."

The process did not remain a war measure, however, but was considerably improved afterwards. Norris,[262] in a fine paper summarizing the prior art in an extensive bibliography, reported on his own process. He claimed to have obtained ammonium sulfate of 95 percent purity, containing 2.5 percent sodium sulfate, 0.22 percent free acid, and 1.5 percent water. The sodium sulfate produced also was of 95 percent purity. Costs were given, which showed the process to be even more advantageous under normal conditions than in war. Molitor [263] described the plant arrangement and the process used by him. Anhydrous sodium sulfate and ammonium sulfate (both technically pure) were produced.

Another half-substituted sulfuric acid proposed and used in making ammonium sulfate is ethylsulfuric acid. This com-

254 Anon., *Chem. Trade J.*, **58**, 342–3 (1916); *Chem. News*, **113**, 175–6 (1916).
255 Gavin, R. J., *Gas World*, **65**, 539–40 (1916); *J. Gas Lighting*, **136**, 545–6 (1916).
256 Société industrielle de produits chimiques, Brit. Pat. 109,814 (1917).
257 Société industrielle de produits chimiques, Brit. Pat. 127,549 (1918). Vis, G. N., U. S. Pats. 1,364,822, 1,366,301–2 (1921).
258 Société industrielle de produits chimiques, Brit. Pat. 136,834 (1918). Vis, G. N., U. S. Pat. 1,366,303 (1921).
259 Fischer, F., and Niggemann, H., *Ges. Abhandl. Kenntnis Kohle*, **1**, 285–8 (1915–6).

260 Dawson, H. M., Brit. Pat. 114,236 (1917); *J. Chem. Soc.*, **113**, 675–88 (1918); *J. Soc. Chem. Ind.*, **38**, 91–101T (1919).
261 Anon., *Gas- u. Wasserfach*, **61**, 91–2 (1918).
262 Norris, W. H. H., *J. Soc. Chem. Ind.*, **40**, 208–12T (1921).
263 Molitor, H., *Chem.-Ztg.*, **50**, 485–6 (1926).

pound is obtained in some coke plants, which recover ethylene from gas as ethyl alcohol with the aid of strong sulfuric acid. The ethylsulfuric acid obtained in the gas-scrubbing operation must be treated with an alkali to recover ethyl alcohol. Vallette and the Compagnie de Béthune [264] proposed using ammonia as the alkali, and thus recovering ammonium sulfate as a byproduct. It would seem that this process would not be applicable to the treatment of coke-oven gas in a saturator but might be feasible with strong ammonia liquor or dephlegmated vapors from the ammonia still.

AMMONIUM HUMATES

A purely organic acid material for the removal of ammonia from gas was proposed in the form of peat and humic acids of various kinds. It was first advocated by de Cuyper [265] at the turn of the century. This inventor proposed to recover ammonia from its compound with peat by heating the mass at temperatures up to 80° C. Anyone who has ever worked with humic acids knows how tenaciously they hold ammonia. The second part of de Cuyper's process is therefore thought to be nonoperative. Kollrepp and Wohl [266] made a similar proposal but purposely worked at temperatures at which moisture would not condense. The product was to be extracted with water or acids to recover ammonia from the ammoniated peat, but the authors also advocated its use as a fertilizer. Lemmermann and Wiessmann [267]

investigated the fertilizing value of ammonium humate and found it to be equal to ammonium sulfate when used as a top dressing but inferior when worked into the soil. Different soils showed different behavior. Wiederhold and Ehrenberg [268] brought ammonia-containing gases into contact with disintegrated lignite or other crude carbonaceous material containing organic acidic substances, and Industrial Research Ltd. [269] did virtually the same thing. Ammonia may be recovered from these masses in the usual manner, or they may be used as fertilizers. Scholl and Davis [270] in recent years took up the ammoniation of peat and came to very favorable conclusions. A nitrogen content as high as 21.7 percent was obtained, of which 70 to 95 percent was in active form. It would seem that this subject should receive more attention, certainly from gasworks which have ready access to peat bogs of high humic acid content or to brown coals of the Kassel Brown type, which are almost pure humic acid.

Other common acids such as hydrochloric, nitric, phosphoric, and carbonic have been proposed and used, but since processes employing them usually start with ammonia liquor, they will be treated in a special section of this chapter as well as in the chapter dealing with ammonia liquor.

PRODUCTION OF AMMONIUM SALTS BY DOUBLE DECOMPOSITION

The processes of the Société industrielle de produits chimiques have already been described. [257, 258] Briefly, they contemplate using niter cake as the absorbing agent to

264 Compagnie de Béthune, Brit. Pat. 197,315 (1923). Vallette, F., *Chimie & industrie*, **13**, 718–21 (1925).

265 De Cuyper, E., Ger. Pat. 70,791 (1893).

266 Kollrepp, A., and Wohl, A., Ger. Pat. 134,-775 (1902).

267 Lemmermann, O., and Wiessmann, H., *Führling's Landw. Ztg.*, **69**, 282–9 (1920); *Chem. Abs.*, **15**, 1054 (1921).

268 Wiederhold, H., and Ehrenberg, C., U. S. Pat. 1,459,703 (1923).

269 Industrial Research Ltd., Brit. Pat. 191,-741 (1923).

270 Scholl, W., and Davis, R. O. E., *Ind. Eng. Chem.*, **25**, 1074–8 (1933).

make a double sulfate of sodium and ammonium, which is decomposed by heat to yield ammonia. Feld [271] absorbed ammonia from gases with the aid of salts so chosen that the corresponding oxides, hydroxides, carbonates, sulfides, and cyanides would on heating expel ammonia from the salts. To the washing solutions there might be added salts of alkalies or ammonia in order to prevent coagulation of the washing liquid. In a typical example, a solution of magnesium chloride containing ammonium chloride was fouled with gas and then regenerated by heating. Almost pure carbon dioxide was first obtained, then carbon dioxide and ammonia. Finally the original magnesium chloride solution was regenerated, and as a result of the operation the ammonia of the gas was obtained in a more concentrated form. The fouling step was expressed by the equation:

$$MgCl_2 + 2NH_4Cl + 2NH_3 + CO_2 + H_2O \rightarrow$$
$$4NH_4Cl + MgCO_3$$
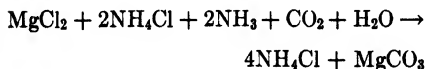
On heating, the reaction is reversed according to the equations:

$$2MgCO_3 + 8NH_4Cl + H_2O \rightarrow$$
$$MgCO_3 \cdot Mg(OH)_2 + 8NH_4Cl + CO_2$$

$$MgCO_3 \cdot Mg(OH)_2 + 8NH_4Cl \rightarrow$$
$$2(MgCl_2 \cdot 2NH_4Cl) + 4NH_3 + CO_2 + 2H_2O$$
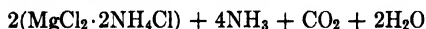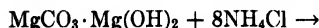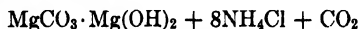
Bergfeld [272] treated gas with the solution of a salt easily oxidized and reduced by the electric current. He obtained free ammonia and sulfur. The process is represented by the following equations:

$$2KI + 2H_2O \xrightarrow[\text{current}]{\text{electric}} I_2 + 2KOH + H_2;$$
$$I_2 + H_2S \rightarrow 2HI + S$$

$$HI + NH_3 \rightarrow NH_4I;$$
$$NH_4I + KOH \rightarrow NH_3 + KI$$

Instead of KI there may be used $Mn_2(SO_4)_3$. The process is more interesting than practical. According to another patent,[273] Bergfeld washed the gas with solutions of salts "which combine with or absorb other substances and hold them until heated to about 100° C." This "hot actification" is very reminiscent of processes for the recovery of hydrogen sulfide from gases, which have become rather prominent. They are described in Chapter 26. Bergfeld proposed removing ammonia from gas by weak or only partially saturated acid compounds such as primary potassium phosphate, fluorides, polyborate, citrate, acetate, or esters with weakly bound acid. Heating of the solutions expels the ammonia and regenerates the original washing liquor. Bone and Finch [274] used primary ammonium phosphate in a very similar manner. Deitz [275] passed gas containing ammonia through a bed of vanadic acid, in the presence of water at temperatures of 30 to 80° C. The solid product on heating to 200 to 250° C liberates ammonia with regeneration of vanadic acid. A still fancier system was devised by the I. G. Farbenindustrie.[276] According to this scheme the gases were brought into contact with microporous hydrophilic absorbents that contained added water. The exhausted mass might be regenerated by a treatment with moist or moistened gases or with steam. The water in the absorbents might contain ammonium nitrate or calcium chloride, and the absorbent might be

[271] Feld, W., Ger. Pats. 176,746 (1902), 185,-419 (1905); U. S. Pat. 837,035 (1906); Brit. Pat. 18,505 (1906); Fr. Pat. 369,258 (1906).
[272] Bergfeld, L., Ger. Pat. 263,905 (1913).

[273] Bergfeld, L., Ger. Pat. 270,204 (1911).
[274] Bone, W. A., and Finch, G. I., Brit. Pat. 222,587 (1923).
[275] Deitz, L. S., Jr., U. S. Pat. 1,849,420 (1932).
[276] I. G. Farbenindustrie A.-G., Brit. Pat. 495,-026 (1938); Fr. Pat. 834,881 (1938).

silica gel or activated alumina. Pressures up to 200 atmospheres could be used. On the same order, but leading to the next group of processes—those using double decomposition—is the idea presented by Jeanprost and Maginot [277] of utilizing base-exchanging compounds such as zeolites to absorb ammonia, pyridine, and other compounds from gas.

Many investigators have tried to bind ammonia in gas by treatment with metal-salt solutions, particularly sulfates. Foremost among these proposals is one utilizing the cheapest sulfate in existence: natural gypsum. It is quite understandable that this intriguing substitute for sulfuric acid received a great deal of attention, especially in countries which have to import sulfur. The difficulties were manifold, and, though it had its start in byproduct ammonia recovery, the process was really not brought to perfection until it had been taken up by the synthetic ammonia industry. Very large German plants are equipped to use either the old-fashioned sulfuric acid or the gypsum process, and, according to private information, they use either, depending on the price of imported sulfur and sulfur ores. This independence in the choice of raw materials has tremendous economic advantages, since the operator is no longer at the mercy of the supplier of raw materials.

Carbonic acid is perhaps the most important factor in the proper functioning of the gypsum process, which in consequence is particularly adapted to indirect ammonia-recovery plants, where the ammonia liquor furnishes the best means of regulating the ammonia-carbon dioxide ratio. However, it may also be used with the semi-direct process.

Bolton and Wanklyn [278] at a very early date suggested that crude coke-oven and blast-furnace gas be cleaned of ammonia by passing it over gypsum. Feld [279] passed gas, from which tar and water had been removed in the usual manner, into a gypsum suspension. Wählert [280] reported on the operation of a plant using the Feld process. After a lull of about 20 years Tunius [281] revived the problem. He figured that coke-oven gas contains more than sufficient carbon dioxide to react with all the ammonia in it, but that ammonia liquor obtained by distillation of the crude does not. He washed the tar-free gas with a suspension of calcium sulfate in a revolving column, using the countercurrent principle, and recovered 98 percent of the ammonia present in the gas. The rest was washed out with water. The process requires careful chemical control and is costly, owing to the necessity of evaporating the ammonium sulfate solution. Tunius believed that in normal times it could not compete with the regular sulfuric acid process. Jackman [282] also took up the idea. He washed the gas with a saturated calcium sulfate solution in a packed tower. The calcium carbonate sludge was drawn off from time to time, and the liquor was evaporated to crystallization. The removal of ammonia from the gas is incomplete in the Jackman process, depending chiefly on the temperature and the free ammonia content of the scrubbing liquor. It amounted to 52.4 percent in a semiplant-scale installation, and the author seemed satisfied that with proper refine-

[277] Jeanprost, C., and Maginot, C., Fr. Pat. 793,958 (1936).

[278] Bolton, F. J., and Wanklyn, J. A., Brit. Pat. 2,709 (1882).

[279] Feld, W., Brit. Pat. 29,752 (1906); U. S. Pat. 851,349 (1907).

[280] Wählert, *J. Gasbeleucht.*, **50**, 815 (1907).

[281] Tunius, G. E., *Gas- u. Wasserfach*, **67**, 91–2 (1924).

[282] Jackman, H. W., *Gas J.*, **175**, 428–9 (1926); *Gas Age-Record*, **60**, 107–8, 116 (1927).

ments in the equipment an almost complete recovery should be attainable. However, such refinements would be economically feasible only in large plants.

The majority of the gypsum processes start from preformed ammonium carbonate, from gases rich in carbon dioxide and ammonia, or from strong ammonia liquor. Earliest in the field was perhaps the Société industrielle de produits chimiques, which took out a number of patents [283] covering various phases of the process. They contemplated all three possibilities but in their latest embodiment proposed to pass ammonia and carbon dioxide into a suspension of gypsum in concentrated ammonium sulfate solution at an elevated temperature. The calcium carbonate was filtered from the hot solution, and solid ammonium sulfate was obtained on cooling, whereupon the cycle was repeated. In this way evaporation of dilute solutions was avoided.

The Badische Anilin und Soda Fabrik [284] worked on the problem at about the same time, and they found the greatest difficulty to be the filtration of the fine carbonate sludge. This was overcome by the use of immersion filters like those employed in gold extraction. The carbonate slime coats the filter with a uniformly pervious film, which remains equally effective on washing with a small amount of water. Wride,[285] reporting on the process, claimed that with a three-stage countercurrent process 95 percent of the ammonia was recovered. A small amount of sulfuric acid was used for neutralization. The chief difficulties were said to arise from the formation of

crusts of calcium carbonate and sulfate in the apparatus.

Neumann [286] made an exhaustive study of the process along physicochemical lines. He calculated the equilibrium constant for the reaction and found that it indicates a theoretical yield of 99.95 percent at 35° C. The temperature has a negligible effect, but the concentration is of considerable importance. The reaction is fast in the beginning, but it slows down quickly and actually takes 15 to 20 hours to go to fair completion. Different forms of gypsum were employed in the tests; it was found that the dihydrate gives an 85 percent yield, the hemihydrate 92 percent, and anhydrite 90 percent. Formation of the double salt "ammon syngenite" was a limiting factor. For practical purposes the anhydrite was recommended.

An anonymous communication [287] reported on the operation of the Oppau plant of the Badische Anilin und Soda Fabrik in which 1,000 tons of gypsum was consumed daily. Carbon dioxide gas was passed into a suspension of gypsum in ammonia liquor contained in a number of cone-bottom tanks equipped with stirrers. The reaction lasted 9 to 10 hours. Volatilized ammonia was recovered by water scrubbing. An ammonium sulfate solution of 25 percent was produced.

Matignon and Frejacques [288] found that with commercial gypsum and concentrated solutions of ammonium carbonate and ammonium sulfate the equilibrium was practically reached after 5 hours' agitation, and the coefficient of transformation was over 96 percent. The velocity of the reaction was studied as a function of the concen-

[283] Société industrielle de produits chimiques, Fr. Pat. 427,065 (1911), Fr. Add. to above 14,046 (1911), Add. 15,307 (1912), Add. to above 16,763 (1913) ; Ger. Pat. 253,553 (1912).
[284] Badische Anilin und Soda Fabrik, Brit. Pat. 27,962 (1913) ; Ger. Pat. 281,174 (1913).
[285] Wride, D. H. B., Chem. Age (London), 2, 82–3 (1920).

[286] Neumann, B., Z. angew. Chem., 34, 441–2, 445–7 (1921).
[287] Anon., Chem. & Met. Eng., 24, 391–4 (1921).
[288] Matignon, C., and Frejacques, M., Compt. rend., 175, 33–5 (1922).

tration of the ammonium carbonate solution, of the size of the gypsum particles, and of the rate of stirring. Fast agitation gave greater reaction speed, as did fine grinding of the solid phase. Ammonium sulfate in the initial solution retarded the completion of the reaction, as did dilution of the ammonium carbonate.

Jackman[282] saturated a 15 percent ammonia liquor with carbon dioxide obtained from flue gases in a packed tower. Gypsum was added to this solution in small quantities at a time, with stirring. Calcium carbonate was filtered off and the solution evaporated to produce solid ammonium sulfate. Hoffman,[289] with gas liquor as a starting material, obtained a 65 percent yield, the salt being 95 percent pure. The product was discolored because hydrogen sulfide attacked the iron evaporator. Parrish[290] discussed the reaction between ammonium carbonate and anhydrite. He pointed out that carbonation and conversion must be carried out in separate vessels if the reaction rate is to be increased and side reactions are to be prevented; he himself used four vessels in series.

Wasilewski and associates[291] investigated the influence of pressure on the process. They used a countercurrent ammonia system and a suspension of gypsum in carbon dioxide and steam (?), and tried pressures of 2 to 3 atmospheres and temperatures of 14 to 120° C. With a ratio of 12 parts of a gas containing 18 percent ammonia to 50 parts gypsum, a 40 percent ammonium sulfate solution was obtained. The recovery of sulfur trioxide contained in the gypsum was 96.5 to 98.5 percent, and the ammonia loss was kept below 0.2 percent.

Teletov and associates[292] studied equilibria and yields of the reaction

$$CaSO_4 + (NH_4)_2CO_3 \leftrightarrows$$
$$CaCO_3 + (NH_4)_2SO_4$$
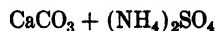
They concluded that: (1) reducing the gypsum particles to a size finer than will pass a screen 40 to 70 mesh per square centimeter does not accelerate the reaction; (2) raising the temperature accelerates the reaction. Equilibrium was reached in 90 minutes at 20° C and in 40 minutes at 50° C.

Gorshtein and Vishnevskii[293] estimated the operating costs of the gypsum process to be from 12 to 20 percent lower, and capital investment to be 25 percent lower, than in the standard sulfuric acid process.

General papers describing one or more technical gypsum processes, their production costs, and their economic possibilities have been published.[151, 294] Muhlert,[161] in a survey of the utilization of nitrogen in coal, stated that the gypsum process has not proved successful in the coke-oven industry except for very large plants. In view of what has been reported above, this is not surprising but would rather be expected.

Though natural gypsum is considered as the raw material in the processes previously discussed, a number of investigators used the calcium sulfate in superphosphate

[289] Hoffman, R. A., *Gas Age-Record*, **61**, 111 (1928).

[290] Parrish, P., *Gas World*, **93**, 564–7 (1930); *Gas Engr.*, **47**, 695–6 (1930); *Inst. Gas Engrs., Communication* **19**, 9–24 (1930).

[291] Wasilewski, L., Kaczorowski, A., and Zabicki, S., *Przemysl Chem.*, **14**, 150–8 (1930); *Chem. Abs.*, **24**, 5942 (1930).

[292] Teletov, T. S., Veleshinetz, A. D., Gurevich, S. M., Dmitrenko, G. I., and Rogacheva, I. A., *Ukrain. Khem. Zhur.*, **7**, 141–68 (1932); *Chem. Abs.*, **27**, 2535 (1933).

[293] Gorshtein, G. I., and Vishnevskii, A. N., *Ukrain. Khem. Zhur.*, **7**, 156–82 (1932); *Chem. Abs.*, **27**, 2535 (1933).

[294] Frydlender, J. H., *Rev. prod. chim.*, **29**, 613–6, 649–54 (1926). Biddulph-Smith, T., *Iron & Coal Trades Rev.*, **116**, 179–80, 222–3 (1928). Waeser, B., *Brennstoff-Chem.*, **11**, 396–8, 418–20 (1930).

or that of phosphoric acid manufacture. These attempts will be described later.

Closely related to the ordinary gypsum process is the idea of Bambach and Company [295] to substitute sulfur dioxide for carbon dioxide and to employ the reaction

$$2NH_3 + SO_2 + H_2O + CaSO_4 \rightarrow$$
$$CaSO_3 + (NH_4)_2SO_4$$
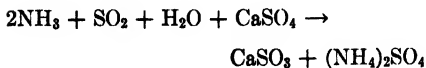
The calcium sulfite thus produced was to be decomposed by means of acids, or acid salt solutions such as niter cake. This process would seem too roundabout to be generally practical.

One other natural sulfate offers some prospects, at least in a few localities: Glauber's salt. Gulinov and Petrov [296] based their proposal on the fact that every winter tens of millions of tons of 98 percent Glauber's salt are washed ashore the Karabugaz bay on the Caspian Sea. They wanted to convert this salt to ammonium sulfate and sodium carbonate by the reactions

$$Na_2SO_4 + 2NH_3 + 2CO_2 + 2H_2O \rightarrow$$
$$2NaHCO_3 + (NH_4)_2SO_4$$
$$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$$
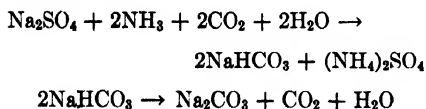
How well the process worked has not been disclosed.

Next in importance to the processes using calcium and sodium sulfates are those using a number of other sulfates, especially of heavy metals. Few ever achieved real success, but they were of decided importance in the development of the industry because they led the way to utilizing the sulfur in the gas for the recovery of ammonia from it.

SIMULTANEOUS RECOVERY OF AMMONIA AND SULFUR

Campbell and Boyd [297] oxidized the hydrogen sulfide of the gas with manganese dioxide and eventually recovered the ammonia in the form of sulfate by absorption in manganese sulfate solution. Iron sulfate found much favor because it is so commonly and cheaply available as pickling liquor from the steel industry and as waste acid from manufacturing operations such as the treatment of titanium ores. Falding [298] took out a number of patents in which he described the use of pickling liquor. He first removed hydrogen sulfide and hydrogen cyanide from the gas before he scrubbed it with the liquor, and after absorption he oxidized the solution in order to convert soluble ferrous hydroxide to the insoluble ferric hydroxide. Ammonium sulfate was recovered from the solution. Feld [299] also employed ferrous sulfate solution, but he precipitated it as iron sulfide. England [300] used ferrous sulfate in a saturator and precipitated it as oxide. Perry [301] employed either ferric sulfate or pickling liquor, and he tried to utilize the precipitate of iron sulfide (with or without ferrous hydroxide) by roasting it to oxide or sulfate. Ammonium sulfate was obtained by evaporation and crystallization in the customary manner. Coleman [302] presented a rather elaborate scheme. The gas was treated with a countercurrent of ferrous sulfate solution so that at the gas inlet there was an excess of ammonia and hydrogen sulfide, and at

295 Bambach & Co., Ger. Pat. 279,953 (1914).

296 Gulinov, V. G., and Petrov, G. V., *Ukrain. Khem. Zhur.*, 6, 137–54 (1931) ; *Chem. Abs.*, 26, 2280 (1932).

297 Campbell, A., and Boyd, W., Brit. Pat. 10,186 (1888).

298 Falding, F. J., U. S. Pat. 961,763 (1910) ; Brit. Pat. 20,245 (1910).

299 Feld,· W., *Z. angew. Chem.*, 24, 97–103 (1911).

300 England, G. W., Brit. Pat. 26,429 (1911).

301 Perry, F., Brit. Pat. 14,079 (1912).

302 Coleman, W. H., Brit. Pat. 20,900 (1912).

the gas outlet an excess of ferrous sulfate. This was made possible by the addition of hydrogen sulfide, ammonia, or ferrous sulfate from later stages of the process. The liquor was heated to insolubilize the cyanogen compounds, excess ammonia and hydrogen sulfide were expelled and returned to the gas, and the precipitate was filtered off. Ammonium sulfate was obtained from the filtrate in known manner, and the filter cake was treated with sulfuric acid in two steps to obtain a neutral iron sulfate solution, insoluble cyanogen-iron complexes, and hydrogen sulfide. The last may be converted to sulfuric acid.

Zinc sulfate proved a little more successful than iron sulfate, probably because under the conditions of its use it is less complicated by the formation of insoluble cyanide complexes. It became rather prominent for a while and may still have good chances in plants of sufficient size. Though the process is normally attributed to Cobb the idea seems to have been voiced first by Fabry. In his earliest patents and in a paper [303] Fabry proposed washing crude coke-oven gas with cold, neutral zinc sulfate solution, making ammonium sulfate and zinc sulfide. The sulfide was dried and roasted to the sulfate, which goes back into the process. Ammonium sulfate was recovered from the solutions in known manner. A later patent and paper [304] contained the suggestion of dissolving the zinc sulfide in sulfuric acid, thus regenerating zinc sulfate and evolving hydrogen sulfide, which could be converted to sulfuric acid. Cobb [305] had substantially the same ideas as Fabry, but he augmented them by an

attempt to overcome the main difficulty of the process—the roasting of the sulfide to sulfate. Apparently a mixture of sulfate and oxide is obtained in a normal roasting operation. Cobb proposed to slurry this mixture with water and to introduce into it the roasting gases and air, in order to convert the oxide portion to sulfate *via* the sulfite. A paper by Curphey [92] pronounced the process technically successful. Cobb himself many years later [306] considered the process sound but thought it applicable only to large plants, because on a small scale the high labor costs involved in the many operations would be prohibitive. The I. G. Farbenindustrie [307] also tried to solve the main problem of the Fabry-Cobb process by treating the zinc sulfide in aqueous slurry at about 180° C under an oxygen pressure of 20 to 30 atmospheres. There would seem to be a far greater chance of technical success with this modification than with the original process, because it would make the conversion more dependable, eliminate drying of the zinc sulfide sludge, and save much labor.

A proposal closely related to the preceding was made by Fritzsche.[308] It contemplated scrubbing the gas with a solution of aluminum sulfate, producing aluminum hydroxide and ammonium sulfate, which was recovered from the solution. The aluminum hydroxide was filtered off and converted to aluminum sulfite by means of sulfur dioxide, and the sulfite was in turn oxidized to sulfate, which went back into the process.

These last processes brought to partial fulfillment the fondest dream of men in

[303] Fabry, R., Brit. Pat. 4,473–4 (1910); *J. Gas Lighting*, **112**, 52 (1910).

[304] Fabry, R., Brit. Pat. 5,667 (1911); *Engrais*, **28**, 551–3 (1913); *Chem. Abs.*, **7**, 4060 (1913).

[305] Cobb, J. W., Brit. Pat. 13,141 (1912); U. S. Pat. 1,108,705 (1914).

[306] Cobb, J. W., *Gas J.*, **188**, No. 3472, *Inst. Gas Engrs. Suppl.*, 45 (1929).

[307] I. G. Farbenindustrie A.-G., Brit. Pat. 288,977 (1927).

[308] Fritzsche, P., Brit. Pat. 25,454 (1911), Ger. Pat. 256,400 (1912).

the gas industry: to utilize the hydrogen sulfide of the gas for the production of ammonium sulfate. It had been realized since the beginning of coal carbonization that there is enough sulfur in the average gas to take care of all the ammonia it contains. To many practical men it was therefore painful to have to buy sulfuric acid while they had to remove hydrogen sulfide from gas at considerable cost and without appreciable return. Naturally, many efforts were made to accomplish this aim fully, but only few were crowned with success. The work of two men in particular has been so outstanding that their names are commonplace in the industry: Feld and Burkheiser.

The early efforts of Feld [299] were directed to using iron sulfate for the absorption of ammonia and hydrogen sulfide, but soon he learned that it was unnecessary to keep adding iron sulfate and removing iron sulfide. Feld found that iron sulfide would dissolve with the aid of sulfur dioxide to form water-soluble salts such as thiosulfate (FeS_2O_3) and tetrathionate (FeS_4O_6). These solutions are capable of absorbing ammonia and hydrogen sulfide, forming the corresponding ammonium salts and iron sulfide. Thus by alternately treating the solutions with coke-oven gas and sulfur dioxide an enrichment with ammonium salts is obtained. When a concentration of 30 to 45 percent ammonium polythionate is reached, the liquor is heated and sulfur dioxide is passed through it, whereupon the polythionates are decomposed with the formation of ammonium sulfate, iron sulfate, sulfur, and sulfur dioxide. The sulfur is separated and part of it is burned to furnish the sulfur dioxide necessary in the process. Iron sulfate is precipitated by passing raw gas through the solution, the iron sulfide is filtered off, and the solution is evaporated to obtain solid ammonium

sulfate. Other salts such as those of zinc or manganese can be used in the process.

The mechanism of this scheme is very involved and embodies a large number of reactions. Feld [309] described them in great detail, listing some twenty-one equations. Other publications on this subject are numerous.[4, 160, 310, 311, 312]

Feld soon recognized that the metal salts were wholly unnecessary for the process, and that he could do just as well by starting with a solution of ammonium polythionates. Owing to the early death of the inventor the development and scientific investigation of this newer phase of the process were left to others. According to Feld's improved process, the original wash liquor was made up of ammonia, sulfur dioxide, and sulfur, and consisted mainly of ammonium tri- and tetrathionate:

$$2NH_3 + SO_2 + S + H_2O \leftrightarrows (NH_4)_2S_2O_3$$

$$2(NH_4)_2S_2O_3 + 3SO_2 \leftrightarrows$$
$$(NH_4)_2S_3O_6 + (NH_4)_2S_4O_6$$
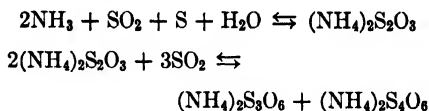
When the gas is scrubbed with this solution it picks up ammonia and hydrogen sulfide according to the equations

$$(NH_4)_2S_3O_6 + 2NH_3 + H_2S$$
$$= 2(NH_4)_2S_2O_3$$

$$(NH_4)_2S_4O_6 + 2NH_3 + H_2S$$
$$= 2(NH_4)_2S_2O_3 + S$$
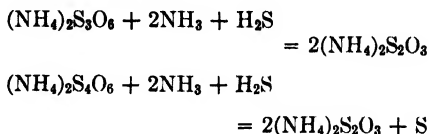
309 Feld, W., *J. Gas Lighting*, **107**, 816–8 (1909); *Z. angew. Chem.*, **24**, 97–103 (1911), **25**, 705–11 (1912).
310 Anon., *J. Gas Lighting*, **107**, 761 (1909). Stavorinus, D., *J. Gasbeleucht.*, **53**, 705–6 (1910). Hurdelbrink, F., *ibid.*, **53**, 956, 61 (1910).
311 Reichel, J., *Stahl u. Eisen*, **33**, 982–7, 1028–30 (1913); *Glückauf*, **49**, 568–72, 616–9 (1913).
312 Feld, W., Ger. Pats. 237,607 (1909), 271,-105, 272,474 (1911), 272,475 (1912), 325,652, 339,612 (1918), 814,627 (1919); Brit. Pats. 3,061 (1909), 10,147 (1912); Fr. Pat. 481,241 (1911); U. S. Pats. 1,011,048 (1911), 1,079,291 (1913).

The thiosulfate solution thus formed is easily regenerated at about 35° C with the aid of sulfur dioxide, ordinary burner gases with 10 to 12 percent sulfur dioxide content being satisfactory:

$$2(NH_4)_2S_2O_3 + 3SO_2 \rightarrow$$
$$(NH_4)_2S_3O_6 + (NH_4)_2S_4O_6$$
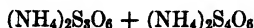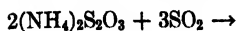
By alternate fouling and regenerating, the ammonium salt concentration of the solution is gradually increased. In consequence, part of it is withdrawn and worked up by heating, which decomposes the polythionates with formation of ammonium sulfate, sulfur dioxide, and sulfur:

$$(NH_4)_2S_3O_6 \rightarrow (NH_4)_2SO_4 + SO_2 + S$$
$$(NH_4)_2S_4O_6 \rightarrow (NH_4)_2SO_4 + SO_2 + 2S$$

The sulfur is filtered off and part of it burned to furnish the necessary sulfur dioxide for the process; the ammonium sulfate solution is evaporated and crystallized. Though the salt thus produced is of excellent purity and low acidity it is likely to turn red on storage, owing to the presence of some ammonium thiocyanate which is also formed in the process.

Raschig and his coworkers deserve the credit for having developed the Feld process on a commercial scale after the inventor's death and for having undertaken its scientific penetration.[313] Raschig pointed out that other thionates, such as the pentathionate, are involved; that arsenites serves as catalysts in the sulfur dioxide oxidation step; and that a ratio of $2NH_3$ for $1H_2S$ is essential for a proper functioning of the process. Many other workers have stressed the scientific angle and have given reviews and accounts of practical operation.[4, 12, 314]

In spite of the tremendous amount of effort and money spent on the development of the Feld process it did not survive in practice (Muhlert[161]). This was due primarily to the fact that the required ratio of $2:1$ for $NH_3:H_2S$ is seldom found in coal-carbonization gases. Even when it normally exists in the average gas, the fluctuations during a day are usually great enough to cause trouble. According to Funcke[314] an excess of hydrogen sulfide makes for safe and satisfactory operation, but a deficiency brings grief. Raschig[313] held a contrary opinion; he thought an excess of hydrogen sulfide more troublesome. He suggested making up for deficiencies by adding sulfur dioxide or ammonia, as the case might be. However, in principle, the Feld process solves the problem of utilizing the sulfur of the gas for the production of ammonium sulfate, and it does it with the cheapest oxidizing agent: air.

Burkheiser, the inventor of the second great process of this group, also used sulfur dioxide but in quite a different manner. His original scheme contemplated the following. Hydrogen sulfide and cyanogen are first removed from the gas by normal dry-box purification with hydrated iron oxide. The fouled oxide is revivified *in situ* with so much air that the iron sulfide is oxidized to sulfur dioxide which is absorbed in ammonium sulfite liquor to form a mixture of sulfite and bisulfite. This solution in turn is used to absorb ammonia from the gas, re-forming ammonium sulfite. When the salt concentration has reached

[313] Raschig, F., Z. angew. Chem., **33**, I, 260–2 (1920).

[314] Espenhahn, E. V., J. Soc. Chem. Ind., **36**, 483–9 (1917). Anon., Gas Age, **42**, 198–9

(1918); Génie civil, **143**, 159 (1918). Sander, A., Chem.-Ztg., **41**, 657–9 (1917); J. Gasbeleucht., **62**, 65–8 (1919). Foerster, F., and Hornig, A., Z. anorg. allgem. Chem., **125**, 86–146 (1922). Funcke, W., Glückauf, **60**, 835–40, 868–76, 897–905 (1924); Gas- u. Wasserfach, **68**, 388–90, 402–5, 417–20, 483–5 (1925). Terres, E., and Overdick, F., ibid., **71**, 49–53, 81–6, 106–10, 130–6 (1928).

saturation, solid salt is precipitated during the ammonia-absorption stage and is removed by centrifuging. This salt, however, is not pure ammonium sulfite, according to Terres and Heinsen,[315] contains varying amounts of ammonium sulfate, because, besides sulfur dioxide, the trioxide is formed in burning the fouled oxide mass, and because the gas always contains some oxygen, which readily oxidizes sulfite to sulfate. To help along this last reaction the centrifuged salt is treated in a rotating drum with hot air, or it is left to oxidize at room temperature, a process which may take several weeks. As it comes from the centrifuge the salt is composed of 2 parts sulfate and 1 part sulfite and was said by Wieler[316] and others to be entirely satisfactory as a fertilizer. Descriptions of this original Burkheiser process are given by several investigators.[4, 159, 160, 311, 317, 318]

The first difficulty arose from the oxidation of the fouled oxide mass, because the high temperatures involved caused rapid loss of activity. To overcome this defect, Burkheiser[319] proposed the use of an iron oxide suspension, filtration of the sulfide, careful oxidation to oxide and free sulfur, separation of the free sulfur from the re-

generated oxide by means of ammonium sulfide, recovery of sulfur from the ammonium sulfide by heating, and oxidation of the sulfur to sulfur dioxide. Detailed accounts of this newer version of the process were given by the inventor's brother[320] and others.[12, 312, 318] Terres and Hahn,[321] after studying the factors underlying the Burkheiser process, came to the conclusion that it was theoretically sound and workable. They gave data on the partial pressures of ammonia and sulfur dioxide over various solutions of ammonium sulfite at various temperatures.

Burkheiser extended and modified his process in various respects. For instance, he realized the disadvantage of producing ammonium sulfite, and therefore proposed to send the sulfur dioxide through a catalyst chamber to convert it to sulfur trioxide. The ammonia removal would then be carried out with a solution of ammonium sulfate-ammonium bisulfate, and the solid salt eventually produced would be pure ammonium sulfate. Ammonium thiocyanate made in his process he proposed to hydrolyze to ammonia, which would boost the overall ammonia yield of the coke plant by about 10 percent. A study of his many patents[322] is suggested for further details. Several patents to other investigators cover a number of minor details; they are merely referred to[323] here. Two papers are worth mentioning, although

315 Terres, E., and Heinsen, A., *ibid.*, **70**, 1157–61, 1193–7, 1217–20 (1927).

316 Wieler, A., *Deut. landw. Presse*, **39**, 847 (1912). Anon., *Saaten Dünger u. Futtermarkt*, **1911**, 219–20; *J. agr. prat.*, **21**, 300–1 (1911); *Betterave*, **21**, 103–4 (1911); *Expt. Sta. Record*, **25**, 328 (1911); *Chem. Abs.*, **6**, 789 (1912). Lewis, A. H., and Marmoy, F. B., *J. Agr. Sci.*, **23**, 1–5 (1933).

317 Bertelsmann, W., *Chem.-Ztg.*, **34**, 986–9 (1911). Wolffram, H., *J. Gasbeleucht.*, **54**, 323–9, 299–305 (1911); *Z. angew. Chem.*, **24**, 513–4 (1911).

318 Moon, P. G. G., *Gas J.*, **188**, No. 3472, *Inst. Gas. Engrs. Suppl.*, 45–52 (1929); *Trans. Inst. Gas Engrs.*, **79**, 294–304 (1929–30).

319 Burkheiser, K., *8th Intern. Congr. Appl. Chem.*, **10**, 63–77 (1912); *Chem. Abs.*, **6**, 3006 (1912).

320 Burkheiser, W., *Gas- u. Wasserfach*, **69**, 765–71 (1926), **70**, 943–5 (1927).

321 Terres, E., and Hahn, E., *ibid.*, **70**, 309–12, 339–43 (1927).

322 Burkheiser, K., Ger. Pats. 212,209 (1907), 215,907, 217,315 (1908), 223,713, 225,461, 235,-870 (1909), 249,001, 254,351, 256,893, 262,979 (1911), 263,593 (1912), 279,262 (1913); U. S. Pat. 973,164 (1910); Brit. Pat. 15,877 (1910).

323 Wolf, F., U. S. Pat. 994,485 (1910). Barth, R., Ger. Pat. 285,157 (1910). A.-G. der Chem. Fabrik Pommerensdorf, Ger. Pat. 281,095 (1913). Sommer, F., U. S. Pat. 1,837,079 (1931).

they are not directly connected with the Burkheiser process. Ishikawa and Murooka [324] made an extensive physicochemical study of ammonium sulfite. They determined its solubility over a wide temperature range, the equilibrium in the system $(NH_4)_2SO_3$-$(NH_4)_2SO_4$-H_2O, the equilibrium in the system SO_2-NH_3-H_2O, and the heats of solution of ammonium sulfite and bisulfite. Shokin, Egorkin, and Khaĭtovich [325] determined the vapor pressures of the components over the system SO_2-NH_3-H_2O.

The one problem arising from the Burkheiser process which has received more attention than any other is the conversion of sulfite and bisulfite to sulfate. This is probably because its scope extends far beyond that of the Burkheiser scheme. Essentially, two reactions are involved: namely, the oxidation of sulfite by atmospheric oxygen, and the auto-oxidation of sulfites by means of the oxygen contained in sulfur dioxide. The first reaction has been known to analytical chemists since time immemorial:

$$2Na_2SO_3 + O_2 \rightarrow 2Na_2SO_4$$
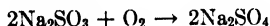
the second was discovered by Barbaglia and Gucci [326] in 1880:

$$6NH_4HSO_3 \rightarrow$$
$$3(NH_4)_2SO_4 + H_2SO_4 + S_2 + 2H_2O$$

Since it is strongly exothermic it often occurs with explosive violence.

Burkheiser [327] attempted the conversion of his sulfite-sulfate mixture by heating it in a screw conveyor in a current of hot air, and Wolf [328] did it similarly except that he kept the salt in a moist condition and at a lower temperature. Stutzer [329] resorted to pressure and oxidized the salt at a temperature at which it dissociates. Collett and Eckardt [330] treated the sulfite solution with pyrite burner gases containing sulfur trioxide, until the salt contained an excess. Danneel and Kuhn [331] employed calcium sulfate as a catalyst to accelerate the oxidation of sulfite solutions and to prevent loss of ammonia. The I. G. Farbenindustrie did a great deal of work on the subject, exclusively on solutions. Evaporation was avoided by adding more salt, or ammonia and sulfur dioxide, to the mother liquor of a preceding operation. [332] The explosion hazard was overcome by passing the sulfite-bisulfite solution through a pipe-still at 150 to 180° C, so that only small amounts of material were in the danger zone at any one time, [333] or by using catalysts, sulfur, selenium, tellurium, or arsenic, which lower the reaction temperature so much (60 to 90° C), and equalize the reaction rate to such an extent, that it cannot become violent. [334] Reaction with air or oxygen was carried out under pressures as high as 20 atmospheres, and in the presence of the catalysts iron, manganese, plat-

324 Ishikawa, F., and Murooka, T., *Science Repts. Tôhoku Imp. Univ., 1st Ser.*, **22**, 201–19 (1933) ; *Chem. Abs.*, **27**, 5235 (1933).

325 Shokin, I. N., Egorkin, I. M., and Khaĭtovich, M. I., *J. Chem. Ind. (U.S.S.R.)*, **15**, No. 7, 10–16 (1938) ; *Chem. Abs.*, **32**, 9409 (1938).

326 Barbaglia, G. A., and Gucci, P., *Ber.*, **13**, 2325–6 (1880).

327 Burkheiser, K., U. S. Pat. 1,034,974 (1912).

328 Chem. Ind. A.-G. and Wolf, F., Ger. Pat. 245,873 (1909).

329 Stutzer, A., Ger. Pat. 255,439 (1913).

330 Collett, E., and Eckardt, M., Brit. Pat. 29,-386 (1910). Collett, E., Brit. Pat. 3,123 (1913).

331 Danneel. H., and Kuhn, E., U. S. Pat. 1,274,247 (1918). Elektrizitätswerk Lonza, Brit. Pat. 105,906 (1917).

332 Bosch, C., U. S. Pat. 1,106,919 (1914). Badische Anilin und Soda Fabrik, Ger. Pat. 270,-574 (1912).

333 Badische Anilin und Soda Fabrik, Ger. Pat. 270,379 (1912). Bosch, C., U. S. Pat. 1,133,086 (1915).

334 Bosch, C., Mittasch, A., and Hecht, L., U. S. Pat. 1,063,007 (1913). Badische Anilin und Soda Fabrik, Ger. Pat. 273,306 (1912).

inum, or cerium deposited on porous carriers of clay, firebrick, pumice, etc.[335] Bosch [336] of the I. G. discussed the mechanism of the reaction and thought it ran *via* thiosulfate and polythionates, though the sum equation is the one given above for ammonium bisulfite. He suggested that by starting with enough neutral sulfite in the solution to neutralize the free acid formed the reaction could be made to yield only sulfate and sulfur. Vorländer and Lainau [337] made a lengthy study of the influence of various catalysts, other salts, acid, and alkali on the oxidation. They found cobalt, iron, nickel, copper, cerium, manganese, and vanadium to have a positive effect, whereas excessive concentrations of H+ or OH− ions, large amounts of salts, and alkali sulfides have a negative effect. A cobalt-sulfito-ammonia complex salt was especially favored as a catalyst. Nitrogen oxides have been used as catalysts for the oxidation of solid sulfite or bisulfite salt or its solutions,[338] though Kachkaroff [339] oxidized entirely with dilute nitric acid. Hodsman and Taylor [340] worked at definite hydrogen-ion concentrations, using iron, manganese, copper, or cobalt catalysts or completing the reaction by electrolysis. Hori [341] used a saturated solution of ammonium sulfate as a carrying medium, employing copper, nickel, or iron as catalyst, and kept the system under oxygen pressure. Von Girsewald and Stahl,[342] using copper, manganese, or iron as catalysts, introduced a mixture of oxygen and sulfur dioxide into sulfite solutions, the gas being in an extremely fine state of subdivision. Sperr [343] introduced the oxidizing air into the lower portion of a narrow column, 20 to 60 feet tall, which contained the ammonium sulfite solution.

It has also been proposed to decompose the ammonium sulfite with sulfuric acid.[344] Sulfur dioxide, thus produced in concentrated form, presumably was to be used for the manufacture of sulfuric acid. Such a proposition would not be unreasonable at all for large plants with a sulfur output corresponding to at least 10 tons of sulfuric acid per day, the smallest economical unit for a catalytic sulfuric acid plant. After all, the catalytic conversion of sulfur dioxide to the trioxide has been perfected to such an extent that it will always be superior to oxidation plans such as those outlined above. Of course, the scheme would be logical only where the sulfur of the gas is obtained in such a manner that sulfur dioxide of insufficient concentration for catalytic conversion is produced.

Although the available literature on the oxidation of ammonium sulfite or bisulfite to sulfate is to be found mostly in patents, a number of scientific publications have also appeared. Foerster and associates [345]

[335] Mittasch, A., and Morowitz, H., U. S. Pat. 1,091,284 (1914). Badische Anilin und Soda Fabrik, Ger. Pats. 273,315 (1912), 276,490 (1913).

[336] Bosch, C., Z. Elektrochem., **24**, 361 9 (1918).

[337] Vorländer, D., and Lainau, A., *J. prakt. Chem.*, **123**, 351–76 (1929); Ger. Pat. 519,048 (1929); U. S. Pat. 1,925,739 (1933).

[338] Naamlooze-Vennootschap de Bataafsche Petroleum Maatschappij, Brit. Pat. 341,570 (1929); Fr. Pat. 707,992 (1930).

[339] Kachkaroff, P., Fr. Pat. 731,922 (1931).

[340] Hodsman, H. J., and Taylor, A., Brit. Pats. 356,283 (1930), 377,959 (1931); U. S. Pat. 1,913,276 (1933). W. C. Holmes & Co., Ltd., Fr. Pat. 717,962 (1931).

[341] Hori, S., U. S. Pat. 1,888,633 (1931).

[342] Metallgesellschaft A.-G., von Girsewald, C., and Stahl, E., Brit. Pat. 350,050 (1930). Von Girsewald, C., and Stahl, E., *Metallgesellschaft. Periodic Rev.*, No. 8, 3–8 (1934); *Chem. Abs.*, **28**, 2877 (1934).

[343] Sperr, F. W., Jr., U. S. Pat. 1,986,899 (1935).

[344] Verein für chemische und metallurgische Produktion, Fr. Pat. 712,754 (1931).

[345] Foerster, F., Lange, F., Drossbach, O., and Seidel, W., Z. anorg. allgem. Chem., **128**, 245–342 (1923).

studied the decomposition of free sulfurous acid, sulfites, and bisulfites to sulfate and sulfur. Terres and Heinsen [346] carried out an investigation of the kinetics of the reaction. They found that the rate of oxidation markedly decreased with an increase of salt concentration. Temperature increases are without much effect on the sulfite, but they increase the rate of bisulfite oxidation. No active catalysts were found; lead, which produced a 10 percent increase, was the best. The authors considered the Burkheiser process in the light of their findings.

Volfkovich and Tzirlin [347] calculated the equilibrium constants for the formation at various temperatures of ammonium sulfate from solid sulfite and the gaseous components, and they studied the oxidation of the solid salt and aqueous solutions with respect to the influence of concentration, temperature, air velocity, catalysts, contact surfaces, etc. The best working conditions were found to be: a temperature of 70° C, low concentrations, low rate of flow, and silica gel as active surface. Manganese, chromium, vanadium, selenium, and copper were not catalysts. Solid salt separated by the Cottrell precipitator was oxidized with greater difficulty than that obtained by the wet method. Volfkovich, Dubovitzkii, and Kryuchkov [348] oxidized ammonium sulfite solutions with nitrogen oxides or with nitric acid. The rate of oxidation was increased by increasing the concentrations of nitrogen dioxide in the gas and of

ammonium sulfite in the solution. There was no loss of nitrogen, but nitric oxide had to be recovered and recirculated. The optimum working temperature was from 42 to 45° C. Kuz'min and Postnikov [349] heated solutions of sulfite and bisulfite to form sulfate and sulfur, and found the reaction to be smooth at low temperatures and in any concentration. Below 200° C thiosulfate, polythionates, and sulfate were formed; above 200° C sulfur was also precipitated. At 300° C sulfate and sulfur were formed with yields of 95 to 99 percent. Concentrated solutions gave greater yields than dilute solutions. Sulfur was discharged from the apparatus in molten form, under pressure.

A number of other processes for the production of ammonium sulfate with utilization of the gas sulfur are more or less developments of the Feld and Burkheiser processes, and many contain elements of both. The process developed by Gluud, Klempt, and Brodkorb,[350] which had become known as the Gesellschaft für Kohlentechnik process, contemplated the following. Ammonia and hydrogen sulfide are removed from the gas by scrubbing with an aqueous suspension of iron hydroxide. The resultant iron sulfide slurry is blown with a mixture of air and sulfur dioxide containing burner gases, or successively by air and sulfur dioxide, whereby ammonium thiosulfate is formed. A solution containing 30 to 35 percent of this salt is withdrawn continuously and decomposed by acid according to the equation:

$$3(NH_4)_2S_2O_3 + H_2SO_4$$
$$= 3(NH_4)_2SO_4 + 4S + H_2O$$
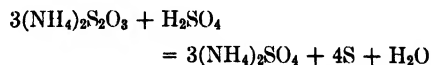
[346] Terres, E., and Heinsen, A., *Gas- u. Wasserfach*, **72**, 994–8, 1022–6, 1050–4 (1929).

[347] Volfkovich, S. I., and Tzirlin, D. L., *J. Chem. Ind.* (*U.S.S.R.*), **6**, 1323–32, 1403–9 (1929); *Chem. Abs.*, **24**, 5942 (1930); *Trans. Sci. Inst. Fertilizers* (*U.S.S.R.*), No. 92, 78–103 (1932); *Chem. Abs.*, **27**, 5899 (1933); *Z. anorg. allgem. Chem.*, **211**, 257–71 (1933).

[348] Volfkovich, S., Dubovitzkii, A., and Kryuchkov, N., *J. Chem. Ind.* (*U.S.S.R.*), **12**, 486–94 (1935); *Chem. Abs.*, **29**, 6869 (1935).

[349] Kuz'min, L. L., Russ. Pat. 44,232 (1935); *J. Chem. Ind.* (*U.S.S.R.*), **13**, 411–8 (1936); *Chem. Abs.*, **30**, 4630 (1936). Kuz'min, L. L., and Postnikov, V. F., *J. Chem. Ind.* (*U.S.S.R.*), **12**, 571–80 (1935); *Chem. Abs.*, **30**, 251 (1936).

[350] Gluud, W., Klempt, W., and Brodkorb, F., *Ber. Ges. Kohlentech.*, **3**, 465–84 (1931).

Part of the sulfur is burned to sulfur dioxide, which is introduced into the iron sulfide slurry in the beginning of the process.

The ammonia : hydrogen sulfide ratio of the gas should be adjusted to 2 : 1. Any excess of ammonia is recovered by an acid wash after the gas is passed through the system; a deficiency is made up by adding ammonia liquor. Hydrogen cyanide should be removed from the gas prior to the process, since otherwise soluble cyanides and thiocyanate contaminate the final product.

The conversion of the thiosulfate to sulfate according to the equation given above was discovered by Gluud and Schönfelder [351] and extended to other acids, such as nitric and phosphoric, by Gluud, Klempt, and Brodkorb.[350] By using acid mixtures, desirable mixed fertilizers can be made, such as sulfate-nitrate or sulfate-phosphate. The decomposition is best carried out at 90 to 100° C, at which temperatures it proceeds smoothly in about 8 hours, with a yield of 98 percent. Higher temperatures increase the speed of reaction, 170 minutes being enough at 150° C, and 45 minutes at 165° C. The mechanism of the reaction and its velocity at different temperatures were investigated thoroughly by Gluud, Klempt, and Hill.[352] It was found to involve the formation of polythionic acids, so that the foregoing equation is actually the sum total of a number of reactions. Descriptions of this interesting process, with cost data and plant diagrams, are given by several investigators,[161, 353] and the various details and

modifications of the process are embodied in a number of patents.[354]

Overdick [355] developed a modification based on the recognition that ammonium tetrathionate, the principal active agent in the Feld process, does not absorb hydrogen sulfide readily unless sufficient ammonia is present; this modification allows the complete removal of both impurities without the addition of foreign ammonia, if excess hydrogen sulfide is present. To accomplish this he washed the gas in several stages. Stavorinus [356] gave the following description of the process. The gas is cooled to 25° C, thus removing tar and part of the ammonia, and then both hydrogen sulfide and ammonia are removed by washing the gas with polythionate liquor in four scrubbers, gas and liquor moving in the same direction. In the first scrubber hydrogen sulfide is taken out to an extent of more than the equivalent of ammonia present; in the second, thionate and hydrogen sulfide react to give free sulfur, aided by the addition of freshly regenerated liquor containing some free sulfur dioxide; the third scrubber receives thionate liquor with an addition of ammonia distilled from the primary cooler condensate, and here the gas is freed of the last traces of hydrogen sulfide; in the final scrubber the last ammonia is taken out by washing with ammonia-free thionate liquor, and the spent liquor then goes to the first scrubber. Regeneration is carried out substantially as in the old Feld process, by heat decomposition at 120 to 130° C. The resultant ammonium sulfate is separated from ammonium thiocyanate,

351 Gluud, W., and Schönfelder, R., *ibid.*, **2**, 23–5 (1926).

352 Gluud, W., Klempt, W., and Hill, H., *ibid.*, **4**, 203–9 (1933).

353 Pasquin, C., *Metallbörse*, **22**, 1149–50 (1932). Weittenhiller, H., *Glückauf*, **74**, 126–31 (1938). Rosendahl, F., *Montan. Rundschau*, **30**, No. 14, 5–7 (1938).

354 Gluud, W., and Schönfelder, R., Ger. Pat. 415,587 (1926). Klempt, W., and Brodkorb, F., Ger. Pat. 568,638 (1929); Fr. Pat. 712,467 (1930). Gesellschaft für Kohlentechnik m.b.H., Brit. Pat. 362,669 (1930).

355 Overdick, F., *Z. angew. Chem.*, **43**, 1048–51 (1930).

356 Stavorinus, D., *Het Gas*, **51**, 19–20 (1931).

which is also formed in the process, by fractional crystallization. The ammonium thiocyanate liquor is converted to ammonium sulfate by autoclaving it at elevated temperatures with sulfuric acid. A number of patents cover the process.[357]

Another process, developed by Hansen, belongs in this group. It has become known as the CAS process because it removes cyanogen, ammonia, and sulfur simultaneously. Koppers described it briefly.[358] In it the gas is cooled in the normal manner of the semi-direct process and is then passed through a scrubber fed with a sulfur slurry, which takes out hydrocyanic acid with the formation of ammonium thiocyanate. Thereafter the gas is washed in several scrubbers with a liquor containing iron thiosulfate, iron polythionates, the ammonium thiocyanate from the hydrogen cyanide scrubber, and suspended iron hydroxide. Ammonia obtained from the primary cooler liquor is added at proper points in these scrubbers. The final scrubber takes out residual ammonia by means of acid-regenerated liquor.

In the main washing operation, iron thiosulfate and iron polythionates take out ammonia and hydrogen sulfide in the ratio of 2 : 1. Any excess hydrogen sulfide is taken care of by the iron hydroxide contained in the liquor, which is indeed put there for that purpose. As a result of these reactions the spent liquor contains ammonium thiosulfate, iron sulfide, and free sulfur.

Part of the reaction mixture is allowed to settle, the clear liquor is treated with sulfur dioxide, and is then heated in a chromium-nickel steel autoclave at about 180° C, whereby the components are converted to ammonium sulfate, sulfur, and carbon dioxide (the last from the thiocyanate). The sulfur is run off in molten form, and the 50 percent ammonium sulfate solution is concentrated in vacuum evaporators.

The settled sludge from the first part of the spent liquor is added to the second part, which is treated with sulfur dioxide in order to dissolve iron sulfide as thiosulfate and polythionate. Undissolved sulfur is filtered off.

A third part of the spent liquor is treated with air, whereby iron sulfide is oxidized to iron hydroxide and sulfur. This slurry is added to the filtrate from the second part, and the mixture is used again as a scrubbing liquor in the gas-purification process.

Because of the complete recovery in this process of cyanogen in the form of ammonium sulfate, the yield of the latter is increased by 8 to 15 percent, depending on the cyanogen content of the gas. However, this very conversion of thiocyanate seems to have increased the difficulties tremendously. The original Feld process already was handicapped by severe corrosion, which became even more severe in the CAS process and finally put it out of existence. At least, Muhlert [161] has stated that it did not survive in practice.

The autoclaving process employed in the conversion of the spent liquors to ammonium sulfate was well worked out. Hansen, Hiller, Voituret, and Züneckel [359] have reported on its scientific aspects. They also have mentioned a method of decomposition which is strongly reminiscent of the one used by Gluud and Schönfelder,[351] described above, except that two moles of

[357] Hansen, C., Ger. Pat. 476,382 (1927). I. G. Farbenindustrie A.-G., Fr. Pat. 666,131 (1928). Overdick, F., Ger. Pats. 558,494 (1930), 576,162 (1933) ; U. S. Pats. 1,868,843 (1932), 1,984,757 (1934) ; Can. Pats. 278,558, 284,390 (1928).

[358] Koppers, H., Gas J., 188, 643–4 (1929).

[359] Hansen, C. J., Hiller, G., Voituret, K., and Züneckel, R., Angew. Chem. 45, 647–50 (1932).

acid are used instead of one. Harnist[360] has given an even better account, treating the behavior of the individual polythionic acid salts and of thiocyanate separately. Hansen and Hiller[361] have described the various reactions available for the conversion of the ammonium thiocyanate formed in the process to ammonium sulfate.

Few descriptions of the technical aspects of the CAS process other than the one by Koppers[358] are available in literature. Salmony[362] has mentioned it briefly and with little detail. Smith[363] reviewed it, largely in the light of British conditions, and came to the conclusion that, though technically entirely sound and workable, it is too complicated, and requires too much technical supervision, to be suitable for British practice. Fieldner[364] has given a short description of it. Hansen, Werres, Hiller, and Voituret[365] have given some general information about its chemistry, and Harnist[360] has disclosed details of apparatus construction.

The patent picture is rather confused because such a large number of patents were taken out on all angles of the process, and because for a while Hansen seems to have worked together with Overdick (see above) on processes which might well have been the forerunners or parts of the Overdick as well as of the CAS process. For this reason they are all grouped together here for the study of those who seek greater detail.[366] Their very number betrays the many difficulties encountered. Some of the patents included in this group seem to be attempts to make the Burkheiser process more workable; others are almost hybrids of the Feld and Burkheiser processes.

A real step forward in the simultaneous recovery of ammonia and sulfur from gas was made by Bähr. He proposed to oxidize catalytically the hydrogen sulfide contained in the gas, so that the sulfur dioxide thus formed could combine with the ammonia in the gas. According to the inventor's earliest description[367] the crude gas was cooled to remove water and some tar, and it was then passed through an electrical tar separator. Ammonia and hydrogen sulfide from the ammonia liquor were returned to the gas. The gas was preheated; some air was added; and then it was passed over a catalyst which converted the hydrogen sulfide to sulfur dioxide and the hydrocyanic acid to ammonia. Since the reaction is exothermic, no extra heat need be supplied, heat exchangers being freely used. When the gas was cooled in a water cooler, much of the ammonium sulfite was deposited. The remainder was taken out by a Cottrell precipitator. The old problem faced by Burkheiser, namely, the oxidation of ammonium sulfite to ammonium sulfate, was circumvented by a'

[360] Harnist, C., *Compt. rend.*, **196**, 1800–2 (1933); *Angew. Chem.*, **46**, 464–7 (1933).

[361] Hansen, C. J., and Hiller, G., *ibid.*, **45**, 581–4 (1932).

[362] Salmony, A., *Chem.-Ztg.*, **53**, 909–10 (1929).

[363] Smith, E. W., *Gas J.*, **188**, 767–8 (1929).

[364] Fieldner, A. C., *U. S. Bur. Mines, Repts. Investigations* **3079** (1931), 13 pp.

[365] Hansen, C. J., Werres, H., Hiller, G., and Voituret, K., *Chem.-Ztg.*, **57**, 361–3, 382–3 (1933).

[366] Hansen, C., Ger. Pats. 504,640, 523,678, 524,792, 526,079, 527,220 (1926), 476,382 (1927); Can. Pats. 278,558, 284,390 (1928);

Fr. Pats. 661,507, 662,709 (1928), 674,187 (1929); U. S. Pats. 1,795,120–1, 1,826,779 (1931), 1,840,579, 1,843,224, 1,852,160–1, 1,854,-511, 1,878,982, 1,885,035, 1,889,894 (1932), 1,894,-252, 1,932,819 (1933), 1,953,478, 1,957,265, 1,957,266–8, 1,968,682, 1,979,934 (1934). I. G. Farbenindustrie A.-G., Brit. Pats. 285,999 (1926), 501,208 (1939); Fr. Pat. 725,926 (1931). H. Koppers A.-G. and Hansen, C. J., Ger. Pats. 507,396 (1926), 513,953, 536,428 (1927), 504,777, 557,989 (1928), 538,392, 545,-829 (1929), 556,519 (1930), 552,289 (1931), 576,158 (1933). H. Koppers A.-G., Brit. Pats. 299,302, 299,765, 301,061 (1927), 316,278 (1928), 309,565, 310,549, 311,725, 314,972 (1930), 356,739 (1931); Fr. Pat. 689,983 (1930).

[367] Bähr, H., *Gas- u. Wasserfach*, **71**, 109–78, 204–11 (1928).

proposal to oxidize it catalytically, in the vapor phase, to a mixture of nitric and sulfuric acids.[368] In a later paper,[369] Bähr gave a great deal of detail on a pilot-plant and on a large-scale installation, as well as numerous illustrations and cost balances. He pointed out that the oxidation of hydrogen sulfide to sulfur dioxide is possible with certain catalysts and great gas velocities, without burning any hydrogen. The hydrogen cyanide is hydrolyzed to ammonia and carbon dioxide, the reaction being complete if the dew point of the gas is at least 40° C. If there is an excess of hydrogen sulfide over the amount permitted by the ratio 1 : 2, some is first washed out with an aqueous sulfite-bisulfite solution, or the gas stream is divided into two parts, one going through the catalyst and the other being washed with the sulfite-bisulfite mixture obtained from the first gas branch. Conversely, if there is an excess of ammonia in the gas some outside sulfur dioxide is added. The salt concentration in the process was taken to 50 to 60 percent, whereupon the solution was either worked up by treatment with various acids to produce different fertilizers, or after acidification was heated at about 130° C in a bath of liquid sulfur to yield sulfate and sulfur. The addition of air to the gas may be a drawback, since about 5 percent of nitrogen is introduced thereby.

A large number of patents cover the interesting process.[370] A study of them re-veals that the original thought of producing only solid ammonium sulfite seemingly was not practical, as a scrubbing with thiosulfate, sulfite-bisulfite, or polythionate solution was used. Thus the solution finally worked up for the production of solid salt contained sulfate, sulfite, bisulfite, thiosulfate, and polythionates. A great deal of effort was expended on finding the proper catalyst for the reaction. There are cited in the various patents the following elements: iron, nickel, copper, cobalt, manganese, zinc, lead, silver, bismuth, tin, tungsten, vanadium, chromium, molybdenum, carbon, boron, silicon, titanium, sulfur, selenium, tellurium, aluminum, alkaline-earth metals, and active carbon. Generally two or three elements were used together.

Short descriptions of the Bähr process, also known as the Katasulf process, have been given by Muhlert and Lorenzen,[371] but Bähr's own papers [367, 369] are so excellent that their study suffices.

As a matter of historical interest a proposal should be cited here which has a certain relation to the Bähr process inasmuch as it treats the gas directly to form ammonium sulfate from the gas components, though it does not employ catalysts. Mackenzie [372] suggested treating moist coke-oven gases with nitrogen oxides in order to oxidize the hydrogen sulfide to sulfur trioxide, which would form ammonium sulfate with the ammonia of the gas. Quite obviously, this scheme would be neither . practical nor economical, since other gas components would be attacked,

368 Bähr, H., Ger. Pat. 566,947 (1927).

369 Bähr, H., Chem. Fabrik, 11, 10–20 (1938).

370 Bähr, H., and F. Siemens A.-G., Brit. Pat. 268,024 (1925). Bähr, H., Ger. Pats. 510,488 (1925), 567,631 (1926), 538,435 (1927), 536,719, 545,627 (1928), 561,559 (1929), 570,243 (1930), 575,134, 576,137, 587,797 (1933), 641,400 (1937); Fr. Pat. 609,931 (1926); U. S. Pats. 1,880,942 (1932), 2,152,454 (1939). F. Siemens A.-G., Brit. Pat. 276,347 (1926); Fr. Pat. 639,693 (1927). I. G. Farbenindustrie A.-G., Brit. Pats. 310,063 (1927), 319,396 (1928), 351,975 (1929), 469,452 (1937); Fr. Pats. 669,421, 38,066 (1929), 699,574 (1930); Ger. Pat. 634,427 (1936). Bähr, H., and Wietzel, G., Ger. Pats. 525,066 (1927), 529,110 (1929).

371 Muhlert, F., Brennstoff-Chem., 10, 487–90 (1929). Lorenzen, G., Z. angew. Chem., 42, 768–73 (1929).

372 Mackenzie, J., Brit. Pat. 10,059 (1914); U. S. Pat. 1,155,753 (1915).

and nitric oxides are too expensive as oxidizing agents.

Much more reasonable are modern proposals to isolate the hydrogen sulfide from the gas and convert it in the usual manner to sulfuric acid. For coke plants of sufficient size this would, no doubt, be entirely feasible, and would constitute the happiest solution of the whole problem of joint recovery of gas sulfur and ammonia. Inasmuch as a contact sulfuric acid plant of 10 tons' daily capacity is an economical unit, a comparatively large number of coke plants in the United States would be eligible for such a scheme. According to a private communication,[373] a coke plant of the Pittsburgh district washes the gas with an alkaline aqueous solution, expels the hydrogen sulfide from the foul liquor by steaming under vacuum, burns the hydrogen sulfide to sulfur dioxide in a regular sulfur burner, catalytically converts the sulfur dioxide to the trioxide, and then uses the acid in the normal saturator operation. The sulfur-removal method in this scheme is the "hot actification system" of Koppers described in Chapter 26. Bähr[374] followed the same line of attack, using solutions of triethanolamine, salts of amino acids, or alkali phenolates as the alkaline liquor for the hydrogen sulfide concentration step.

AMMONIUM PHOSPHATES

Although ammonia is practically always recovered from gas as the sulfate, the production of other salts has not been totally neglected. Several attempts in that direction have been related. Inasmuch as the main use for byproduct sulfate was in the fertilizer industry, it was natural to think of combining ammonia with superphos-

phate, an acidic fertilizer material. In this way sulfuric acid would serve the double purpose of converting natural phosphate rock into available phosphate and binding ammonia of the gas. Later investigators went a step further and also tried to utilize the waste gypsum contained in superphosphate. Others went in the opposite direction, converting the rock phosphate completely to phosphoric acid and producing regular ammonium phosphate. That there is enough acidity in superphosphate to bind all the ammonia produced in coal carbonization is evident from the statement by Baumann[375] that 60 percent of the world's production of sulfuric acid is used in the manufacture of superphosphate, and only 16 percent for ammonium sulfate.

The earliest proposal was made by Bolton and Wanklyn,[376] who merely added superphosphate to ammonia liquor and evaporated the slurry. Bolton and Wanklyn[278, 377] passed tar-free gas over superphosphate in dry boxes. Bunte[378] investigated this process thoroughly on a plant scale and came to the conclusion that, if properly carried out, it is entirely feasible, shows no disadvantages in the operation of the gas plant, and yields a higher return for the ammonia than when the ammonia is in the form of gas liquor. The product analyzed 7.5 percent ammonia and 0.46 percent thiocyanate. Gerlach,[379] in a lengthy paper on the ammoniation of superphosphate, gave a detailed analysis, and pointed out that, owing to the presence of gypsum, the end product contains calcium phosphate and ammonium sulfate. However, the cal-

[373] The Koppers Co., Pittsburgh, Pa.

[374] Bähr, H., U. S. Pat. 2,045,747 (1936), Ger. Pat. 672,414 (1939). I. G. Farbenindustrie A.-G., Fr. Pat. 757,745 (1933).

[375] Baumann, J., *Chem.-Ztg.*, **44**, 346–7 (1920).

[376] Bolton, F. J., and Wanklyn, J. A., Brit. Pat. 5,173 (1880).

[377] Bolton, F. J., and Wanklyn, J. A., Ger. Pat. 16,788 (1882).

[378] Bunte, H., *J. Gasbeleucht.*, **25**, 282–7 (1882); *Dinglers Polytech. J.*, **245**, 40–2 (1882).

[379] Gerlach, U., *Z. angew. Chem.*, **29**, I, 13–4. 18–20 (1916).

cium phosphate is in a form which, though not water-soluble, is soluble in water saturated with carbon dioxide. Fertilizing tests showed that the product is superior to physical mixtures of calcium phosphate and ammonium sulfate.

Jacob, Hill, Ross, and Rader [380] investigated the chemical composition of citrate-insoluble residues from superphosphates and ammoniated superphosphates, and came to the general conclusion that ammoniation decreases the solubility in neutral citrate solution. Keenen,[381] on the other hand, contended that practically no reversion of phosphate to the insoluble form occurs, provided that the amount of ammonia used does not exceed one mole per mole of water-soluble phosphate. With more than two moles ammonia there is formed a mixture of diammonium phosphate, ammonium sulfate, calcium sulfate, and tricalciumphosphate. Luckmann [382] reviewed various methods for the ammoniation of superphosphate. His data showed that the fixation of an increasing amount of ammonia converts an increasing amount of soluble phosphate to the insoluble form. In spite of this he was of the opinion that the savings effected are often more important than the tendency to render the phosphates less immediately available.

A considerable number of patents were taken out in this field. Some of them merely provide suitable apparatus; others cover details of the process. Some start from superphosphate of special compositions; others utilize mainly the gypsum portion of it, or, to avoid reversion to insoluble phosphate, they carefully regulate the amount of ammonia added. When utilization of the gypsum part is desired there must be added carbon dioxide besides the ammonia, and we then are dealing with processes such as were outlined above under ammonium sulfate manufacture. These patents are referred to for special study.[383]

Other investigators went a step beyond superphosphate and utilized phosphoric acid itself. Caro and Scheele [384] made crude phosphoric acid containing some excess sulfuric acid, and used it for the production of ammonium phosphate containing 20 to 25 percent ammonia and 40 to 45 percent phosphoric acid in soluble form. Thau [170] referred to a process by Pease in which three moles of sulfuric acid were used to bind six moles of ammonia and thus to make two moles of soluble phosphate. This would mean that actually triammonium phosphate was made from phosphoric acid first produced from phosphate rock.

Direct treatment of phosphate rock has also been attempted.[385] The process contemplated converting an aqueous suspension of the ground rock with carbon dioxide and ammonia. If it is workable, and if Baumann's [375] figures are correct, this process would have a profound effect on

380 Jacob, K. D., Hill, W. L., Ross, W. H., and Rader, L. F., Jr., *Ind. Eng. Chem.*, **22**, 1385–92 (1930).

381 Keenen, F. G., *ibid.*, **22**, 1378–82 (1930).

382 Luckmann, H., *Kunstdünger u. Leim*, **32**, 131–3, 165–7, 199–202, 235–8 (1935); *Chem.* Abs., **29**, 8205 (1935).

383 Grahn, E., and Bunte, H., Ger. Pat. 47,601 (1889). Gaillot, M. L., and Brisset, P., Fr. Pat. 375,792 (1907). Pease, E. L., and Tyrer, D., Brit. Pat. 253,572 (1925). Stockholm Superfosfat Fabriks Aktiebolag, Brit. Pat. 264,867 (1926). Stackable, E. R., Brit. Pat. 293,942 (1927). Colbjörnsen, B., Swed. Pat., 64,885. Liljenroth, F. G., Swed. Pat. 67,057 (1929). Hagens, J. F. C., Rosenstein, L., and Hirschkind, W., U. S. Pat. 1,699,393 (1929). The Koppers Co. of Delaware, Fr. Pat. 728,826 (1931). Sperr, F. W., Jr., Brit. Pat. 394,666 (1933); U. S. Pat. 1,980,010 (1934). Harvey, E. W., U. S. Pat. 1,948,520 (1934). Oehme, H., U. S. Pat. 1,949,129 (1934). Shoeld, M., U. S. Pats. 1,980,006–8 (1934), 2,003,560 (1935).

384 Caro, N., and Scheele, T. E., Brit. Pat. 26,726 (1908).

385 Compagnie des mines de Vocoigne, Noeux et Drocourt, Fr. Pat. 650,109 (1927).

the economy of every country, since it would save three-fourths of all the sulfuric acid now produced. Lloyd and Kennedy [386] treated phosphate rock with ammonium bisulfate, separated the gypsum formed, treated the resultant solution with ammonia, separated triammonium phosphate, and then added sulfuric acid to reform bisulfate, which was put back into the process.

From the preceding discussion, it appears that the production of ammoniated superphosphate in a coke plant might offer some advantages. It allows diversification of production to plants which hitherto could make only sulfate, and it should offer worthwhile savings, if the manufacture is not unduly complicated.

AMMONIUM CARBONATES

The utilization of the carbon dioxide of the gas in the recovery of its ammonia content has also received a fair amount of attention. Though there is ample carbon dioxide in the average gas, the direct recovery of ammonium carbonates has proved difficult, owing to the high vapor pressure of these salts with respect to their components. One method, in which the gas is cooled to low temperature, has been referred to in connection with the indirect ammonia-recovery process. Another method was described by Key and Etheridge.[387] The ammonia from all the gas was concentrated into one fraction; this fraction was detarred, then enriched by distilling into it the ammoniacal liquor produced from the whole of the gas, and the mixture was passed through a saturated solution of ammonium bicarbonate. Only gases containing more than 1.6 percent car-

bon dioxide could be treated in this manner.

By far the best method for the production of ammonium bicarbonate employs ammonia liquor as a starting material. It is first converted into concentrated ammonia liquor, which is then neutralized with carbon dioxide obtained in the distillation of the weak liquor. Solid bicarbonate is thus precipitated and is recovered in the usual manner by centrifuging. A survey of the literature and details of the process, which was largely worked out by Gluud and his associates, is to be found in Gluud and Jacobson's book,[12] in one of Gluud's papers,[388] and in Chapter 32 of this book.

The process has been in operation in a German coke plant since the early '20's and has given entire satisfaction. The value of ammonium bicarbonate as a fertilizer has been established beyond reasonable doubt, and it offers some advantages over other fertilizers, inasmuch as it adds valuable carbon dioxide to the soil instead of the ballast sulfuric acid.[375, 389, 390]. Nevertheless, it has not been widely adopted, probably because it loses ammonia even at room temperature. Proper packaging minimizes the loss considerably, but neither it nor treatment of the salt with waxes, resins, or other salts would seem to overcome this fault entirely.[390] In the past this loss of ammonia might easily have been serious and even prohibitive, but with relatively cheap synthetic ammonia available conditions are quite different. The price of ammonia is down to such a low level that the loss of some of it in storage and shipment does not matter much. Often it should be cheaper to use the carbon dioxide of the

386 Lloyd, S. J., and Kennedy, A. M., U. S. Pat. 1,816,051 (1931).

387 Key, A., and Etheridge, A. H., *Gas World*, **99**, 425–7 (1933); *Gas J.*, **204**, No. 3676, *Inst. Gas. Engrs. Suppl.*, 4–5, 44–54 (1933).

388 Gluud, W., *Ber. Ges. Kohlentech.*, **1**, 127–51, 320–44 (1922).

389 Bosch, C., *Z. angew. Chem.*, **31**, Pt. 3, 654 (1918). Reinau, E., *Chem.-Ztg.*, **43**, 449–51, 469–72, 489–91 (1919).

390 Gluud, W., *ibid.*, **46**, 693–7, 715–7 (1922).

gas as an acid component and lose some of the ammonia than to buy sulfuric acid and save it all.

There is another angle to the production of ammonium bicarbonate: it offers the chance to produce urea, the concentrated, ideal nitrogen fertilizer, by the reactions $NH_4HCO_3 \rightarrow NH_4CO_2NH_2 \rightarrow (NH_2)_2CO$. Although urea so far has been produced only by large chemical manufacturers, there is no reason why it could not be made in a coke plant of sufficient size. Some literature on this subject is to be found in Gluud and Jacobson's handbook.[12]

A number of older proposals for the manufacture of ammonium carbonate from ammonia liquor and from salts such as ammonium chloride and sulfate have only historical interest. They are ably presented by Lunge-Köhler.[4]

AMMONIUM CHLORIDE

Ammonium chloride is another salt of considerable importance, particularly since it is invariably produced in the coking of coal. Damon[391] stated that for each 0.1 percent chlorine in coal (English coals range from 0.002 to 0.355 percent chlorine) there is produced 3.37 pounds of ammonium chloride per ton of coal; this amount is equivalent to about 25 percent of all the ammonia produced from the coal. Some coals, like those of the Saxony district in Germany, show a particularly high chlorine content, as much as 15 times that of a normal coal,[4] and it exists in the coal largely in the form of sodium chloride. Several investigators have tried to increase the natural production of ammonium chloride by mixing chlorides with the coal before coking. Ostwald[114] added magnesium or calcium chloride and reported a quanti-

tative recovery of the ammonia as chloride. Christenson and Hedman[392] closely followed Ostwald but used chiefly common salt. They recovered the ammonium chloride either by water washing or, in dry form, by cooling the distillation gases to a temperature just above that at which the water and other vapors condense. Such a practice could be of value if the coking and byproduct equipment were not affected, and if the quality of the coke were not decreased. The problem may be worthy of further study.

The ammonium chloride naturally produced in coking operations is recovered directly only in the Brunck and Otto direct ammonia-recovery processes. There it contaminates the ammonium sulfate, and Otto[393] attempted to obtain it from the saturated liquor by fractional crystallization. It was said to be obtained in an almost pure state.

More frequently, however, ammonium chloride is obtained from the ammonia liquors produced in the semi-direct and indirect processes. Attention has already been drawn to the interesting indirect recovery described by Tramm.[163] Other processes which contemplate repeated circulation of ammonia liquor through the collecting main are described in Chapter 32.

Production of ammonium chloride in the manner in which ammonium sulfate is made, i.e., by scrubbing the gas with hydrochloric acid, has not been favored in the past. The reasons probably are the high cost of the acid compared with that of sulfuric acid, the greater difficulty of handling it, and the corrosiveness of the acid and its ammonia salt. It was proposed by

391 Damon, W. A., *Ann. Rept. Alkali &c. Works, 1929*, **66**, 21–8 (1930) ; *Chem. Abs.*, **24**, 4611 (1930).

392 Christenson, O. L., and Hedman, B. A., Brit. Pat. 159,817 (1921).

393 C. Otto & Co. G.m.b.H., Ger. Pat. 239,997 (1910) ; Ger. Appl. O. 7042 (1911).

Main and Galbraith [394] in 1884 and was taken up again in 1938 by Heterich,[395] of the I. G. Farbenindustrie, who proposed the use of solutions containing less than 5 percent, and preferably about 2 percent, of the acid. In this dilution, losses of the volatile acid can probably be avoided.

Attempts to use common chlorides such as magnesium and calcium chloride for direct recovery of ammonia from the gas apparently have not led anywhere. Mond [128] suggested such a method, but his plants actually used sulfuric acid, and Niggemann [396] flatly asserted that it was not feasible.

The employment of the Solvay process for the production of ammonium chloride in coke plants has assumed some importance, particularly the modification introduced by Gluud and Löpmann. Since these processes have to start from strong ammonia liquor, or from ammonium bicarbonate, they are described in Chapter 32. A good description and literature survey is also to be found in Gluud and Jacobson's handbook,[12] and other appraisals of ammonium chloride production by the soda process are to be found in papers by Biddulph-Smith [294] and Freitag.[397]

Conversion of ammonium sulfate to chloride by double decomposition with alkali chlorides has been practiced off and on, especially in semi-direct coke plants. Because of the ability of ammonium chloride to sublime, either the wet or the dry method can be used. The wet method was common in the past, but the dry has gained in favor.

Naumann [398] used an excess of sodium chloride and such concentrations that the final hot liquor contained less than 75 parts of ammonium chloride per 100 parts of water. A solution of 80 parts ammonium sulfate in 100 parts water was stirred at a temperature of at least 70° C with an excess of finely ground salt. After 1 to 2 hours the solution was separated from the solid phase and cooled to room temperature, whereupon ammonium chloride crystallized out. The mother liquor was returned to the process. Freeth and Cocksedge [399] used equivalent quantities of ammonium sulfate, worked at 103° C, filtered off the sodium sulfate formed, and cooled to 30° C to separate pure ammonium chloride. Schmidtborn and Harnish [400] started from ammonium sulfate and potassium chloride. The solid potash salt was introduced into a boiling solution of ammonium sulfate, and the potassium sulfate formed was filtered off while hot. Ammonium chloride of 98 to 99 percent purity was finally obtained by fractional crystallization. Dominik [401] made a study of the reaction and came to the conclusion, on experimental and theoretical grounds, that a proportion of 69 parts ammonium sulfate, 61 parts sodium chloride, and 100 parts water and a temperature of 60° C would be the best conditions for a successful conversion. Freitag,[397] in his critical survey of ammonium chloride manufacture, stated that in the Freeth and Cocksedge process the solution must not be cooled below 39° C if contamination with sodium sulfate is to be avoided, since 33° C is the transition point of anhydrous sulfate to Glauber's salt. He gave an exact procedure, which was said to yield an ammonium

394 Main, R., and Galbraith, W., Brit. Pat. 10,448 (1884).

395 Heterich, A., Ger. Pat. 663,570 (1938).

396 Niggemann, H., *Ges. Abhandl. Kenntnis Kohle,* 1, 289–90 (1915–6).

397 Freitag, R., *Ind. Eng. Chem.,* 24, 1235–7 (1932).

398 Naumann, E., Ger. Pat. 196,260 (1908).

399 Freeth, F. A., and Cocksedge, H. E., Brit. Pat. 26,263 (1909) ; Ger. Pat. 226,108 (1910).

400 Schmidtborn, T. H., and Harnish, H. H., U. S. Pat. 330,155 (1885).

401 Dominik, W., *Przemysl Chem.,* 5, 257–63 (1921) ; *Chem. Abs.,* 16, 2967 (1922).

chloride of 99 to 100 percent purity if followed rigorously.

The direct sublimation of molecular mixtures of ammonium sulfate and sodium chloride has been described by several investigators. Klaus and Basler[402] heated such a mixture, to which 1 percent sodium bisulfate had been added, and claimed to have obtained ammonium chloride of 99.88 percent purity. Continentale A.-G. für Chemie[403] heated the mixture in a stream of oxidizing gas, such as oxygen, or with an admixture of peroxides, nitrates, chlorates, etc., and claimed the production of pure white, sublimed ammonium chloride and calcined sodium sulfate.

Details on a number of the double decomposition processes mentioned above are given by Lunge-Köhler,[4] who also mention several other processes which start from ammonium sulfite and ammonium carbonate respectively.

The uses for ammonium chloride are as yet limited. It should be a good fertilizer. Kuyper[404] proved in extensive field tests on sugar cane that it is as good as sulfate, and he found its physical characteristics to be better since it was not deliquescent—an important advantage in the tropics. Numerous other references on its value as a fertilizer as given by Gluud.[12] A fair tonnage of the salt is consumed in the manufacture of dry cells and by steel plants.

AMMONIUM NITRATE

Ammonium nitrate is the last great ammonium salt to be considered. Its recovery by scrubbing the gas with nitric acid has rarely been considered, though Heterich[395] did propose it. The volatility of the acid, and possibly its action on other gas constituents, must have been discouraging factors. Feld[405] attempted to produce it by treatment of the gas with nitrates of alkalies and alkaline earths, believing that a modified Solvay soda process would take place. However, Lunge-Köhler[4] reported the reaction to be incomplete.

Much more numerous and more successful were the attempts to obtain ammonium nitrate by double decomposition of natural nitrates with ammonia products of the coke plant. Colson[406] described the use of sodium nitrate instead of sodium chloride in the ammonia soda process. The proposal seemingly never got anywhere. Moreover, since it needs concentrated ammonia liquor, it would be of no help to all those plants that make ammonium sulfate by the semi-direct process. Yet those plants are the ones which in times of national emergencies would like to sell their ammonia in the form of nitrate.

Roth[407] converted ammonium sulfate with Chile saltpeter in alcoholic solution, either under reflux or in an autoclave at 120 to 140° C. Only ammonium nitrate is soluble in the alcohol and was recovered from it. Benker[408] carried out the same reaction in an aqueous solution, froze out Glauber's salt, and recovered the nitrate from the mother liquor. Craig[409] did not depend on fractional crystallization; he evaporated the reaction mixture to dryness and separated the nitrate from it with liquid or strong aqueous ammonia, in which the nitrate is soluble but not the sulfate. Naumann[410] added more refinements to

[402] Klaus, F., and Basler, R., Ger. Pat. 482,916 (1925).

[403] Continentale A.-G. für Chemie, Brit. Pat. 235,552 (1924).

[404] Kuyper, J., Arch. Suikerind., 31, 1–4 (1923); Chem. Abs., 17, 1524 (1923).

[405] Feld, W., Ger. Pats. 177,172, 178,620 (1906); U. S. Pat. 839,741 (1906); Brit. Pat. 5,776 (1906).

[406] Colson, A., J. Soc. Chem. Ind., 29, 187–92 (1910).

[407] Roth, C., Ger. Pat. 48,705 (1889).

[408] Benker, F., Ger. Pat. 69,148 (1893).

[409] Craig, G., Brit. Pat. 5,815 (1896).

[410] Naumann, E., Ger. Pat. 166,746 (1905).

the process, first separating sodium sulfate from the hot reaction mixture, then on partial cooling sodium ammonium sulfate, and finally on low cooling ammonium nitrate. Caspari, Nydegger, and Goldschmidt [411] gave exact directions as to ratios, temperatures, and procedures. Hulin,[412] using calcium nitrate and ammonium sulfate, carried out the reaction in autoclaves at 120° C or above, with preheated solutions of the reactants.

The conversion of the dry material has also been reported. Roth [413] fused sodium nitrate with ammonium sulfate at temperatures of 160 to 200° C, using as much as 100 percent excess of the sodium nitrate. The lower layer is solid sodium sulfate; the supernatant liquid is molten ammonium nitrate. Lennox [414] also fused a mixture of sodium nitrate and ammonium sulfate but distilled the ammonium nitrate under vacuum, at about 200° C. Heating above 230° C must be avoided.

More important than all these indirect methods for the production of ammonium nitrate is the direct oxidation of ammonia to nitric acid and its neutralization with ammonia liquor. The idea of having the ammonia of the gas furnish its own acid in the form of nitric acid is a fascinating one, but in spite of the fact that the method was developed in a coke plant it has never been adopted to any great extent by the gas industry. The chief reason probably is that on account of its hygroscopic qualities ammonium nitrate is not considered a good fertilizer. Furthermore, strong ammonia liquor is needed for the process, and thus semi-direct plants cannot use it.

Ostwald [415] deserves the credit for having developed the process, which contemplates essentially passing ammonia with air over a platinum catalyst. The nitrous oxides are washed out of the reaction mixture in water scrubbers, and a nitric acid of about 45 to 50 percent results. A pure ammonia liquor, free from sulfur compounds, is necessary, because platinum catalysts are easily poisoned by such impurities. For details the reader is referred to Lunge-Köhler [4] and to a paper by Waeser,[416] who has given an excellent survey of the art, with a very complete bibliography.

RECOVERY OF AMMONIA IN GAS PURIFICATION AND TAR DISTILLATION

So much for the direct recovery of ammonia from coal-carbonization gases. Only two minor points remain to be discussed. When the gas leaves the normal absorption apparatus, be it the water scrubbers in the indirect system, the ordinary sulfuric acid saturator, or the scrubbers in the Feld, Burkheiser, and similar processes, there is always a very small amount of ammonia left in the gas. It is left there because complete absorption is generally uneconomical, and because it is beneficial in the removal of hydrogen sulfide by the iron oxide in the dry boxes. Ammonium salts are therefore found in all fouled or "spent" oxide masses. Williams [417] noted that an average English spent oxide contained ammonium compounds in the following proportions: ferric ammonium ferrocyanide, 3.80; ferrosoferric ammonium ferrocyanide, 2.50; ammonium sulfate, 2.06; and ammonium thiocyanate, 1.30 percent, re-

411 Caspari, E., Nydegger, O., and Goldschmidt, A., U. S. Pat. 864,513 (1907).

412 Hulin, P. L., Fr. Pat. 480,150 (1916).

413 Roth, C., Ger. Pats. 53,364 (1890), 55,155 (1891), 149,026 (1904).

414 Lennox, R. N., Ger. Pat. 96,689 (1898).

415 Ostwald, W., U. S. Pat. 858,904 (1907); Brit. Pats. 698,830 (1902), 7,909 (1908).

416 Waeser, B., Chem.-Ztg., 44, 838–40 (1920).

417 Williams, H. E., The Chemistry of Cyanogen Compounds, P. Blakiston's Son & Co., Philadelphia, 1915, 423 pp.

spectively. If the spent masses are worked up for the recovery of cyanogen compounds, the ammonia is recovered eventually as sulfate, thiocyanate, or free ammonia. Williams[417] reported on such recovery, as did Waguet.[418] Others have gone so far as to recover all the nitrogen, including that contained in the cyanogen compounds, in the form of ammonia and its salts. Such a proposal was made, for instance, by Simonin,[419] who tried to hydrolyze the cyanogen compounds by distillation with caustic soda.

On the whole, recovery of ammonia from spent oxides is of no immediate practical importance and is unlikely to become more important in the future, as coke plants switch from oxide purification to the modern liquid purification schemes.

Of a little greater importance is the ammonia that leaves the coke plant as liquor emulsified with the tar. Woodward[420] wrote an interesting paper on the subject. He pointed out that it may be recovered both from liquor which settles out on top of the crude-tar storage tank, and, very profitably, from the aqueous fraction obtained in distillation. In a plant where the total amount of water distilled from tar per year averaged about 700,000 gallons, about 85,500 pounds of 20 percent ammonia liquor could be recovered. Sometimes ammonium chloride gets into the tar-distillation equipment, with more or less serious consequences. Corrosion caused in this way was one of the factors against the adoption of the Brunck and Otto direct ammonia-recovery systems. Spalteholz[421] reported on a stoppage caused by ammonium chloride in tar distillation. He overcame it by introducing a small amount of moist steam during the naphthalene period and the first part of the anthracene period.

ECONOMICS OF AMMONIA RECOVERY

At the beginning of coal carbonization the production and recovery of ammonia were desirable and profitable, and every effort was made to increase them; but conditions changed with the advent of synthetic ammonia. Prices have drifted lower and lower, until many small gas works and coke plants have found it a losing proposition to take ammonia out of the gas. Some plants have found relief by selling crude ammonia liquor to farmers—this is dealt with in Chapter 32—but such an outlet is not available in many districts. It is small wonder that efforts have been made either to prevent the formation of ammonia during carbonization or to destroy it afterwards. What a contrast between old and new! Mond hoped to become wealthy, and did so, by increasing the ammonia yield; modern inventors hope to find a bonanza by destroying it. Doubtless the man who finds an easy way of accomplishing this aim will make his fortune. Hellmann[422] proposed to pass hot coal-distillation gases over catalysts to break down their ammonia content. The catalysts could be glowing iron borings. The Hamburger Gaswerke[423] passed the mixture of ammonia and steam, obtained by distilling gas liquor, through a bed of glowing coke in a gas generator to yield a gas mixture of high hydrogen content.[424]

Synthetic ammonia probably could be made in this country from cheap natural gas for less than 2 cents per pound, and possibly for less than 1.5 cents. This price

417 Waguet, P. P., *Rev. prod. chim.*, **24**, 397–404 (1921) ; *Chem. Abs.*, **15**, 3198 (1921).

419 Simonin, H., Brit. Pat. 20,504 (1909).

420 Woodward, C. R., *Met. & Chem. Eng.*, **18**, 299–301 (1918).

421 Spalteholz, W., *Chem.-Ztg.*, **46**, 544 (1922).

422 Hellmann, O., Ger. Pat. 625,739 (1936).

423 Hamburger Gaswerke G.m.b.H., Ger. Pat. 641,267 (1937).

424 Thau, A., *Gas Times*, **14**, No. 171, 30–3 (1938).

level is such that byproduct plants would lose money through the recovery of ammonia. Beebe [425] in an economic study based his calculations on a price of 6.5 cents per pound, and Battin [426] in a similar study came to the conclusion that a price of 4.9 cents per pound is the zero line for profits.

The seriousness of the situation has been generally recognized,[151, 364, 425, 426, 427] but few remedies are available. Faults often prevalent in byproduct sulfate, such as discoloration, caking, and acidity, can be overcome, and methods for the accomplishment of that aim have been pointed out above, but diversification of production is next to impossible except in plants using the indirect process. There is almost unanimity of opinion that the manufacture of one ammonia product only is the greatest single handicap of the industry, for if only one product is offered for sale it cannot take advantage of the up- and down-trends of the chemical markets. Under these conditions the producer is at the mercy of the buyer. This is probably the chief reason why a number of modern, large German plants have returned to the indirect recovery process which has acknowledged disadvantages, but allows the manufacture of whatever happens to command the best market price. Practically all writers on these economic problems are agreed, therefore, that it would be best to manufacture strong ammonia liquor, which in turn could be made into any desired ammonium salt. Parrish [151, 428] very sensibly suggested that the ammonia liquor from a number of plants within a radius of 40 miles be col-

lected and worked up together at a central chemical plant. This should be possible, particularly in heavily industrialized districts with their great concentration of coking facilities, but for isolated small coke and gas plants such a plan would offer no solution. Only small hope can be seen in suggestions to find "new outlets" for ammonia. Such new uses, if they take any sizable tonnage, would only rarely receive substantial patent protection, and would therefore be immediately subject to exploitation by the producers of synthetic ammonia, so that no useful end would be served.

Analytical methods have not been dealt with in this chapter, because the art is so well known and standardized that it would have amounted to a mere repetition. Excellent information on this subject can be obtained from Gluud and Jacobson,[12] Keller,[429] Parrish,[146] and the *U. S. Steel Chemists' Handbook*.[430]

A survey of the development of the byproduct ammonia industry in the United States is contained in Table XXI.

RECOVERY AND UTILIZATION OF CYANOGEN FROM GASES

Although ammonia is the most important nitrogenous compound in carbonization gases, from the standpoint of quantity as well as of economic value, cyanogen (hydrocyanic acid, HCN) nevertheless has not been completely forgotten. In fact, its recovery has been on the minds of fuel technologists for many decades. The intricate chemistry of cyanogen compounds and the lack of markets, however, have

[425] Beebe, A. M., *Am. Gas J.*, **129**, 39–41 (1928).

[426] Battin, W. I., *ibid.*, **129**, 35–6 (1928).

[427] Taylor, R. C., *Gas J.*, **164**, 44–6 (1923); *Gas World*, **79**, 306–9 (1923).

[428] Parrish, P., *Inst. Gas Engrs., Commun.* **213** (1939), 72 pp.; *Chem. Abs.*, **23**, 6564 (1939).

[429] Keller, K., *Laboratoriumsbuch für die Kokerei- und Teerproduktenindustrie der Steinkohle*, Wilhelm Knapp, Halle, 1923, 128 pp.

[430] United States Steel Corporation, Chemists' Committee, *Sampling and Analysis of Coal, Coke, and By-Products*, Carnegie Steel Co., Pittsburgh, 3rd ed., 1929, 334 pp.

TABLE XXI

PRODUCTION OF AMMONIA FROM COAL IN THE UNITED STATES, EXPRESSED IN TONS OF AMMONIUM
SULFATE, AS REPORTED IN VARIOUS SOURCES

Year	Barrett [431] *	Mineral Re- sources [432] ‡	Census and Mineral Re- sources [433, 432] §	Cen- sus [433] ‡	Mineral Re- sources [432] ‖	Tariff Com- mission [434] ¶
1901	27,279					
1902	36,124					
1903	41,873	40,425				
1904	54,664	52,739				
1905	65,296	63,400				
1906	75,000 †					
1907	99,309	97,166				
1908	83,400	81,437				
1909	106,500					
1910	116,000					
1911	127,000					
1912	165,000					
1913	195,000					
1914	183,000					186,150
1915	250,049	249,439				
1916	288,265					
1917	325,670	324,670				
1918	379,278	378,328				
1919	403,223					
1920	449,463					
1921	358,500					
1922	476,761	475,762				
1923	603,363			602,200	575,363	
1924	569,622				544,623	559,050
1925	664,019			650,000	639,019	651,170
1926	715,976				690,976	699,780
1927	742,460			734,100	695,850	724,550
1928					798,887	798,550
1929				849,000	856,214	863,020
1930					769,022	763,600
1931			568,550		569,986	570,890
1932					356,208	360,050
1933			441,730		420,283	439,440
1934					479,911	503,240
1935			545,312		535,250	548,300
1936					694,342	
1937					753,216	
1938					518,383	
1939					676,802	
1940					832,109	

* Includes production in coke ovens plus an estimated value for that in "coal-gas, bone-carbonizing, etc."

† Estimated.

mitigated against universal adoption of available recovery schemes.

As pointed out in the beginning of this chapter, cyanogen is formed essentially from ammonia and carbon or carbon compounds at high temperatures, and the quantity produced is tied up with such factors as oven construction, oven heats, and moisture content of the coal charge. Though some figures have been given above on the yield in pounds per ton of coal carbonized, particularly in relation to the ammonia yield, a few figures on the actual content in the gas might not be amiss.

Leybold [435] was one of the first to make careful determinations of cyanogen in gas; he found it to contain 89 and 116 grains per 100 cubic feet as it came from the collecting main of a gasworks. Drehschmidt [436] reported 90 grains and Nauss [437] 93 grains per 100 cubic feet (gasworks). Feld [438] carried out a more extensive investigation, testing the gas after it came from the tar separators. He reported: for German gasworks 96 to 149 grains per 100 cubic feet, for an English plant 103, for French retorts 99. Jorissen and Rutten [439] of the Amsterdam gasworks found 81 grains per 100 cubic feet, and Ritzinger [440] 311 grains per 100 cubic feet expressed as $K_4Fe(CN)_6$. Bertelsmann [441] thought that retort gas contained from 88 to 109 grains per 100 cubic feet, while coke-oven gas had a maximum of only 66. Gluud and Klempt,[442] using more refined methods of analysis, reported for German coke plants only 21 to 53 grains per 100 cubic feet, which may have been due to the high moisture content with which coal is customarily coked in German coke plants. Mezger [443] found for a very modern German gasworks 50 grains per 100 cubic feet, and Offe,[444] anywhere from 26 to 87, with an average of 26 to 35. For American practice a figure of 60 grains per 100 cubic feet is a good average for coke ovens maintained at normal heats.

The quantities of cyanogen involved seem at first sight insignificant and not worth bothering with. However, assuming an annual gas production of 700 billion cubic feet and the average of 60 grains per

431 *The Production of Sulphate of Ammonia for 1915–16, 22–27,* The Barrett Company, 40 Rector Street, New York, N. Y.

432 U. S. Department of the Interior, Geological Survey, *Mineral Resources of the United States, 1907–23,* U. S. Government Printing Office, Washington, D. C., 1908–26. U. S. Department of Commerce, Bureau of Mines, *Mineral Resources of the United States, 1924–31,* U. S. Government Printing Office, Washington, D. C., 1927 33. U. S. Department of Interior, Bureau of Mines, *Minerals Yearbook, 1932–41,* U. S. Government Printing Office, Washington, D. C., 1933–42.

433 U. S. Department of Commerce, Bureau of the Census, *Biennial Census of Manufactures, 1923–35,* U. S. Government Printing Office, Washington, D. C., 1926–38.

434 U. S. Tariff Commission, *Chemical Nitrogen,* Report 140, 2nd Series, U. S. Government Printing Office, Washington, D. C., 1937.

435 Leybold, W., *J. Gasbeleucht.,* **33,** 336–41 (1890).

436 Drehschmidt, H., *ibid.,* **35,** 221–6, 268–70 (1892).

437 Nauss, A. O., *ibid.,* **45,** 953–7 (1902).

438 Feld, W., *ibid.,* **45,** 933–40 (1902).

439 Jorissen, W., and Rutten, J., *ibid.,* **46,** 716–9 (1903).

440 Ritzinger, *ibid.,* **46,** 44–7 (1903).

441 Bertelsmann, W., *Die Technologie des Cyanverbindungen,* R. Oldenbourg, Munich and Berlin, 1906, 332 pp.

442 Gluud, W., and Klempt, W., *Ber. Ges. Kohlentech.,* **2,** 269–309 (1929).

443 Mezger, R., *Gas- u. Wasserfach,* **70,** 165–70 (1927).

444 Offe, G., *ibid.,* **71,** 222–4 (1928).

‡ Includes production in the byproduct coke industry and in the manufactured-gas industry.

§ Includes production in the byproduct coke industry (Bureau of Mines) plus that in the manufactured-gas industry (*Census*).

|| Includes production in the byproduct coke industry and in city gasworks.

¶ Includes production in coke ovens and gasworks.

100 cubic feet, the annual output of cyanogen in the United States amounts to the stupendous figure of 30,000 tons from coal carbonization only, and the figure might be augmented considerably if blast furnaces were taken into consideration. Obviously, if every coke plant in the United States were to recover cyanogen and sell it in the form of cyanides, the consequences to the established market would be disastrous. Therefore, the prospect of big profits cannot be the incentive for removing cyanogen from gas today any more than in the past. Certainly, there was a time at the end of the last century when cyanides brought good money. Cyanide leaching of gold ores had just been invented, and there was not enough to go around. However, increase in the production of synthetic cyanide followed, and soon the prices were at a point at which recovery plants just about broke even. In spite of these conditions not only was existing equipment kept operating, but new facilities were installed in a number of plants, even where plant managers felt sure they would not make much of a profit.

CORROSIVE ACTION OF HYDROCYANIC ACID

One might ask why anyone would want to take cyanogen out of the gas, in the absence of public regulations requiring its removal, if no money was to be made thereby. The answer is a simple one. Hydrocyanic acid, though only a weak acid, is one of the most corrosive substances known in its effect on iron equipment, owing to its strong tendency to form complex iron salts. Its destructive action is greatly augmented by the presence of water, oxygen, or hydrogen sulfide; since normal coal gas always carries water vapor, ideal conditions for corrosion are offered at almost any point from the carbonizing retort to the customer's appliances.

Bueb [445] was probably the first to point this out, at the beginning of the present century. He mentioned especially the attack on gas holders and gas meters. Salm [446] also considered gas-holder and gas-meter corrosion of primary importance, and he cited as proof his experience that meters were practically destroyed in 4 to 5 years. The sediment in the meter water analyzed 60 percent iron and 24 percent cyanogen. For many years Salm had not experienced any troubles, because ammonia was not completely washed from the gas and thus promoted almost complete cyanogen removal in the oxide boxes, but after an overhauling of his ammonia system his equipment losses became so serious that he installed a cyanogen-recovery plant.

Scheuer,[447] in a general survey of cyanogen removal from gas, also referred to its destructive action on gas meters and holders. Donath [448] reported his investigation of a badly corroded ammonia-still section, which he found to have been completely converted to Prussian blue and graphite. Nauss [437] found a Prussian blue content of 2 percent in the lime sludge of an ammonia still, due, no doubt, to attack by the ammonium cyanide of the ammonia liquor. Ritzinger [440] gave disastrous corrosion of gas holders as the reason for his adopting a cyanogen-recovery system, and he stated that he would have installed it even though it yielded no financial return. Albrecht [449] reported gas meters quickly destroyed by hydrogen cyanide in the gas. Drory [450] added governors to the list of corroded equipment, but he considered the

445 Bueb, J., *J. Gasbeleucht.*, **42**, 469–73 (1899), **43**, 747–50 (1900), **46**, 81–3 (1903).
446 Salm, *ibid.*, **43**, 750–1 (1900).
447 Scheuer, *Z. angew. Chem.*, **14**, 603–7 (1901).
448 Donath, E., *J. Gasbeleucht.*, **44**, 880–1 (1901).
449 Albrecht, A., *ibid.*, **46**, 101–5 (1903).
450 Drory, E., *ibid.*, **46**, 143–4 (1903).

preservation of gas meters to be most significant. He found that the capital investment for the cyanogen-recovery plant was compensated for by increased capacities of coolers and ammonia scrubbers.

Kaysser [451] considered corrosion to holders, meters, and mains so important that he took out a number of patents specifically for the destruction of hydrogen cyanide. Thau,[227] in an investigation of ammonium sulfate discoloration, traced it to cyanogen corrosion of ammonia-still sections and of the piping from the still to the saturator. His remedy was to keep the system hot enough to prevent condensation of moisture. Mueller [452] was quite aware of the corrosive action of cyanogen on all iron equipment, including house pipes and services. McLeod [453] was probably the first to write a special paper on the subject of service-pipe corrosion; he also emphasized the corrosive action of hydrogen cyanide. An anonymous paper [454] claimed that ammonium cyanide is a potent factor in causing corrosion of ammonia- and benzol-distilling plants. Kersting,[455] who devoted a whole paper to rust deposits in gas mains and services, pointed out as one of the consequences the poor gas pressures resulting from the accumulation of rust in service risers and extensions. He considered hydrogen cyanide the most important cause of the troubles, and in analyzing a rust sample he found 11.36 percent ammonium ferrocyanide. Bertelsmann,[456] in a broad survey of cyanogen recovery, stated that intangible gains, such as the preserva-

tion of meters, would make cyanogen recovery advisable even if direct profits were negligible.

Taplay and Parkinson [138] and Taplay [457] also attributed corrosion of mains and services primarily to hydrogen cyanide, and they urged its removal, particularly from high-pressure systems. Parkinson [458] took up the same question in a committee report on the life of gas meters. Minot [459] gave corrosion of gas holders, meters, and mains as his justification for a preliminary removal of cyanogen as ammonium thiocyanate. Williams, Colman, Richardson, and Gluud [460] have written very interesting papers devoted entirely to the problem of corrosion in the gas industry. They all are agreed that hydrogen cyanide is at least partly responsible, although they differ as to the extent and the mechanism. In some of these papers the interrelationship of hydrogen cyanide, carbon dioxide, oxygen, water, and ammonia in the reactions involved is pointed out.

Seymour [461] saw one of the chief advantages of the Koppers Seaboard purification system (for hydrogen sulfide) in the fact that it removes cyanogen at the same time. He found meter deterioration completely cured after the installation of the plant. Sperr [462] pointed out the same thing in a paper dealing with the Koppers Seaboard process, and he also found important savings in gas-distribution costs. In a later

[451] Kaysser, O., Ger. Pats. 211,237 (1908), 218,949 (1909).

[452] Mueller, M. E., J. Gas Lighting, 112, 851–5 (1910); Proc. Am. Gas Inst., 5, 231–51 (1910).

[453] McLeod, J., Gas J., 114, 903–5 (1911).

[454] Anon., Gas World, 58, 667 (1913).

[455] Kersting, A., Am. Gas Light J., 104, 339–41 (1916).

[456] Bertelsmann, W., J. Gasbeleucht., 62, 205–7 (1919).

[457] Taplay, J. G., Gas J., 150, 583–7 (1920); Gas World, 72, 481–5 (1920).

[458] Parkinson, B. R., ibid., 76, 548–53 (1922); Gas J., 158, 834–9 (1922).

[459] Minot, M., Am. Gas J., 115, 386–8 (1921); Chimie & industrie, 6, 135–40 (1921).

[460] Williams, H. E., Gas J., 162, 725–6 (1923). Colman, H. G., ibid, 162, 794 (1923). Richardson, B., ibid., 162, 348–50 (1923), 164, 515–6 (1923); Gas World, 79, 468–70 (1923). Gluud, W, Ber. Ges. Kohlentech., 1, 169–71 (1923).

[461] Seymour, F. W., Gas Age-Record, 50, 765–7 (1922).

[462] Sperr, F. W., Jr., ibid., 52, 553–8 (1923).

paper on gas dehydration,[463] Sperr elaborated on these points, emphasizing that customer appliances also were affected, and pilot lights might be stopped completely. The expenses involved are not only renewal of corroded equipment, but also the costs of testing, adjusting, and repairing meters, losses of gas through leakage, and other items. If the gas were made noncorrosive the large-diameter cast-iron mains could be replaced by small-diameter, cheap steel mains. A drip obtained by compressing gas to 50 pounds and cooling to normal temperature showed 31 grains per gallon ammonium thiocyanate and 15 grains ammonium ferrocyanide. Engler[464] made hydrogen cyanide partly responsible for the corrosion of gas holders, putting it on a par with oxygen. Mezger,[443] in a study on economic considerations involved in the removal of cyanogen from gas, summed up, as the reason for its removal, the destruction of gas holders, mains, governors, and metering devices. A crude-light-oil tank, when repaired after 5 years of service, showed a deposit of 2,860 pounds of a solid substance (6.6 percent of its original weight) containing 23.1 percent Prussian blue.

Schwarz[465] added to the list of cyanogen damage its poisoning of certain catalysts used in liquid hydrogen sulfide purification systems. Parker,[466] in connection with gas dehydration, called attention to the fact that, in the absence of water, hydrogen cyanide will not cause corrosion on bright surfaces of iron and steel. Nübling[467] found that cyanogen removal paid

financially, as well as indirectly by elimination of corrosion of the distribution system. Downing[468] established that rather small quantities of hydrogen cyanide in the gas are able to corrode even galvanized services.

A fair amount of work has been done to clear up the picture of cyanogen corrosion. Ott and Hinden[469] have tested numerous types of pipes with gas of varying hydrogen cyanide concentration. Large numbers of photographs and colored illustrations give a visual idea of the effect. Stavorinus[470] cited an interesting investigation by Hicks, who gave the corrosion rates of gas mains shown in Table XXII.

TABLE XXII

CORROSION RATES OF GAS MAINS[470]

Type of Gas	Ounces Loss per Year per Square Foot Area
Normal moist city gas	0.0262
Normal moist city gas with higher cyanogen content	0.246
Gas free of oxygen, carbon dioxide, and cyanogen	0.0656
Dry city gas	0.0049
Dry city gas free of carbon dioxide and cyanogen	0.0

In a later paper, Hicks[471] estimated the corrosion of Portland City gas mains as 0.001 pound per year per square foot surface. The yearly total of iron consumed was calculated to be 9,500 pounds, equivalent to about 10 tons of Prussian blue. A number of corrosion deposits were ana-

[463] Sperr, F. W., Jr., *ibid.*, **58**, 551–3 (1926).
[464] Engler, R., *Gas- u. Wasserfach*, **68**, 475–8 (1925).
[465] Schwarz, S. C., *Western Gas*, **3**, 118–9 (1927).
[466] Parker, J., *Gas J.*, **178**, 361–2 (1927).
[467] Nübling, R., *Gas- u. Wasserfach*, **73**, 909–18 (1930).

[468] Downing, R. C., *Proc. Am. Gas Assoc.*, **1936**, 699–702.
[469] Ott, E., and Hinden, F., *Monats.-Bull. Schweiz. Ver. Gas- u. Wasserfach.*, **1927**, No. 1–2, 18 pp.; *Chem. Abs.*, **21**, 2550 (1927).
[470] Stavorinus, D., *Het Gas*, **48**, 70 (1928); *Gas- u. Wasserfach*, **71**, 736 (1928).
[471] Hicks, J. F. G., *J. Phys. Chem.*, **35**, 893–904 (1931).

lyzed and found to contain from 7.4 to 91 percent of Prussian blue. He came to these conclusions: (1) hydrogen cyanide, although not a cause, is the chief contributory factor in the internal corrosion of gas mains, carbonic acid and oxygen following in order; and (2) hydrogen cyanide has the greatest intensity of effect and is first in order of priority of attack. Prussian blue is the final product in the corrosion of iron in the interior of gas mains. Pieters [472] determined the corroding effect of hydrogen cyanide in ammonia-still vapors, when they were washed with a slurry of finely divided iron in sodium carbonate solution (95° C) in order to produce ferrocyanide. He found that the rate of corrosion depended on the composition of the metal (Table XXIII). Pieters therefore

TABLE XXIII

CORROSION RATES OF VARIOUS METALS BY HYDROGEN CYANIDE [472]

Metal	Loss in Ounces per Square Foot per Year
18–8 Avesta chromium-nickel steel	0.0052
Monel	0.0034
N.C.T. 3	0.0018
Cast iron	0.0029
Sheet iron	0.0047
V2A steel	0.0047
Cast iron with 1.5 percent nickel	0.0054
Cast iron with 3.0 percent nickel	0.0045

recommended cast iron as the construction material for his scrubbers. Recently, the detrimental effect of cyanogen has been pointed out by Stief [473] and by Murphy.[474] Murphy has made an especially valuable contribution, finding that in conjunction

[472] Pieters, H. A. J., *Brennstoff-Chem.*, **18**, 397–8 (1937).

[473] Stief, F., *Gas- u. Wasserfach*, **82**, 574–7 (1939).

[474] Murphy, E. J., *Gas Age*, **84**, 28–7 (1939).

with mercaptans as little as 0.4 grain per 100 cubic feet of gas is enough to corrode brass appliance pilots. If the gas is free of mercaptans as much as 2 grains is considered permissible.

CYANOGEN REMOVAL IN OXIDE BOXES

However, corrosion of metal equipment is not the only ill effect of cyanogen in gas. In the final purification step, in which iron oxide is used to remove hydrogen sulfide from the gas, the cyanogen binds a certain amount of oxide with the formation of various complex iron cyanides. This iron oxide is irrevocably lost for sulfide purification, thus necessitating more frequent changes of boxes, and a corresponding purchase of fresh material. Moreover, in spite of their sulfur content of 40 to 50 percent, the spent oxides which contain iron cyanides are not useful for the manufacture of sulfuric acid. Bueb [445] pointed out that if cyanogen is removed a better utilization of oxides is obtained, the sulfur content of the spent oxides is higher, and hydrogen sulfide removal is better. Ledig [475] also observed the greater efficiency of the dry boxes; he was able to purify 70 percent more gas with the same amount of oxide. Keppeler [476] used only 75 percent of the number of boxes he had to use before cyanogen removal, and the correspondingly smaller space requirement proved of great importance to him. Mueller,[452] Bertelsmann,[456] and Minot [459] recognized that cyanogen recovery lessens the load on oxide purifiers. Other writers have given more specific information. Thus Schwarz [465] claimed a 33⅓ percent higher oxide utilization, and Mezger [455] found 37 percent. Downing [468] came to the conclusion that the cost of removing the hydrogen cyanide by iron oxide

[475] Ledig, E., *J. Gasbeleucht.*, **43**, 750 (1900).

[476] Keppeler, G., *ibid.*, **47**, 245–8 (1904).

is equal to the cost of removing the hydrogen sulfide, so that a very substantial benefit would be derived from its prior removal.

TOXICITY OF HYDROGEN CYANIDE

A point of comparatively minor importance is the well-known toxicity of hydrogen cyanide. Bueb [445] called attention to the toxic qualities of the water in gas holders, and Wehmer [477] traced to its cyanogen content the poisonous effect of coal gas on the root systems of trees. The effect may be delayed and may not become apparent until the end of the winter rest-period.

DISTRIBUTION OF CYANOGEN IN GASWORKS

For an appropriate consideration of the various cyanogen-recovery or -removal methods proposed or in existence, it is desirable to know just what happens to the cyanogen contained in the crude gas coming from the collecting mains as it passes through the various pieces of plant equipment to the ultimate consumer. Since hydrocyanic acid is an extremely water-soluble compound, being in fact miscible in all proportions with water, it would be expected to be found wherever the gas is cooled sufficiently to deposit water, or where it is washed with water or aqueous solutions. Thus it should be present in primary-cooler liquor, in the ammonia liquor of the indirect ammonia-recovery process, in the final cooler water (where direct final cooling is employed), in the water of gas holders, and in the various drips of the distribution system. It should be present especially wherever an ammoniacal liquor is obtained, since owing to its acidic nature it should combine with ammonia to form ammonium cyanide. Furthermore, because of its great affinity for iron compounds, it

should be found in the oxide purification masses. However, its low boiling point (26° C) and correspondingly high vapor pressure should favor its being carried on by the gas stream, and the presence in the gas of large quantities of carbonic acid (which is a much stronger acid than hydrocyanic acid) should tend to expel it from its union with ammonia.

Strangely, comparatively few data on these questions are available in the literature, though the references given above on the problem of cyanogen corrosion indicate that technologists were well aware of the presence of hydrocyanic acid at various points. It is, of course, perfectly true that distribution figures which would be generally applicable could not be given, because such operating conditions as the temperature of the primary coolers, the kind and number of ammonia scrubbers, the amount of water used in the scrubbers, and the concentrations of ammonia, carbonic acid, hydrogen sulfide, and hydrogen cyanide vary tremendously from plant to plant.

Leybold,[435] Drehschmidt,[436] Lewis,[478] and Nauss [437] have reported figures for the distribution of hydrogen cyanide in gasworks, and their data are summarized in Table XXIV. Powell [479] found distribution of cyanogen in various gases to be as shown in Table XXV. Scheuer [447] pointed out that one-third to one-quarter of the cyanogen contained in crude gas is likely to be found in the city gas mains. The high absorption in the ammonia scrubbers led Nauss to experiment with them. He took three of the four ordinary scrubbers out of the circuit and left only the fourth one (an "intensive" scrubber). Although the ammonia removal remained almost as good

[477] Wehmer, C., *Ber. deut. botan. Ges.*, **36**, 460–4 (1918); *Chem. Abs.*, **13**, 2897 (1919).

[478] Lewis, G. P., *J. Gas Lighting*, **69**, 1049–53 (1897).

[479] Powell, A. R., *Am. Gas Assoc. Monthly*, **4**, 621–7 (1922).

TABLE XXIV

DISTRIBUTION OF HYDROGEN CYANIDE IN GASWORKS

Gas	Grains HCN per 100 Cubic Feet		Gas	Percent Removal	
Leybold [435]					
From collecting main	88.9	116.2	In coolers	8.02	3.76
After coolers	81.8	111.8	In ammonia scrubbers	6.55	1.62
After ammonia scrubbers	75.9	109.9	In dry boxes	56.15	71.45
After dry boxes	26.0	26.9	In holder	19.55	7.67
In holder	8.6	18.0		.	
Drehschmidt [436]					
Before coolers	90.1	....	In coolers	9.27	....
After coolers	81.7	76.9	In ammonia scrubbers	5.87	2.67 .....
After ammonia scrub-			In oxide boxes	66.71	..... 35.47
bers	76.4	74.5 61.6	In holder	9.22	....
After oxide boxes	16.3*	..... 29.7†			
In city main	8.0	....			
Lewis [478]					
After retorts	84–132 Average 108		In condensers	About	3
After condensers	82–127 Average 105		In ammonia scrubbers	About	3
After ammonia scrub-			In purifiers		78.7
bers	80–125 Average 102				
After last purifier	16–18 Average 17				
Nauss [437]					
After one tar separator		91.8	In tar separators		24.29
After all tar separators		69.5	In ammonia scrubbers		23.33
After last ammonia scrubber		48.1	In dry boxes		47.62
After dry boxes		4.4			

* Fresh iron oxide.
† Mass used repeatedly.

TABLE XXV

DISTRIBUTION OF CYANOGEN IN VARIOUS GASES [479]

Gas	Vertical Retorts	Water Gas	Coke Oven with Oxide Purification	Coke Oven with Soda Purification
		grains per 100 cubic feet		
(Outlet of exhauster)				
Inlet to intensive scrubber	44	Trace to 1.3	(25.6)	(46–47)
Inlet to purifier	19	Trace to 1.3	12.3	2.5
Inlet to meter (between purifier and				
light oil scrubber)	14.7	Trace to 1.3		
Outlet of light oil scrubber	7.3	Trace to 1.3	4.6	0.0

as before the change was made, only 1 percent of the original cyanogen was removed. Ritzinger [440] reported that 39.4 percent of the cyanogen was removed with the ammonia liquor.

Mezger [443] disclosed that in his plant 21.3 percent of the cyanogen went into the ammonia liquor, 57.78 percent into the spent oxide, and 20.92 percent remained in the gas to be distributed. Feld [438] asserted that from 40 to 75 percent of the cyanogen was retained by the dry boxes; Lewis [478] found the figure to be about 50 percent; and Anon. [81] contended that under favorable conditions even 80 to 90 percent may be thus retained. Proteus [480] claimed a removal of 60 to 70 percent by dry box operation, and TerNedden [481] found 42 percent of the total cyanogen in the ammonia-absorption stage, and 55 percent in the oxide boxes.

From the foregoing discussion it appears that the primary coolers may remove up to about 10 percent of the total cyanogen, the ammonia scrubbers from 1 to 40 percent, the oxide boxes generally 50 to 60 percent, and the gas-holder water up to 20 percent. A retention of about 20 percent by the ammonia liquor of indirect processes is probably a good average. Semi-direct plants, of course, have to reckon only with the content of the primary cooler liquor.

The great influence of the type of ammonia scrubber and the method of scrubbing is manifest from the findings of Nauss. Little is known about the other factors, but an inkling of the importance of carbon dioxide may be had from the study of a paper by Lenze and Rettenmaier [164] on the cooling of gas to low temperatures. The ammonia liquor obtained at tempera-

tures of -10 to $0°$ C would be expected to contain large quantities of ammonium cyanide. As a matter of fact, Lenze reported it to be "an almost pure 30 percent solution of ammonium carbonate." The amount of cyanide in the liquor was exceedingly small, being only 0.3 percent hydrogen cyanide. Seemingly, the presence of large quantities of carbonic acid completely prevented an absorption of hydrocyanic acid.

REMOVAL OF HYDROGEN CYANIDE

In the early days of the industry of coal carbonization, cyanogen was recovered only incidentally to the removal of hydrogen sulfide from the gas. Clegg and Philips, as cited by Bertelsmann,[441] treated the gas with milk of lime and with solid lime respectively, and a small amount of the hydrogen cyanide was thereby fixed as thiocyanate and to a much lesser extent as calcium ferrocyanide. Since McFarlane [441] found only 0.12 percent cyanogen in a spent lime, this process can have no more than an historic interest, the hydrogen cyanide being neither removed nor recovered in this manner.

A little later, Philips [441] proposed the use of an aqueous suspension of iron oxide for the purification of gas, and Croll [441] advocated dry iron oxide, which was to be regenerated by roasting. Neither process became successful, and it was not until Laming [441] produced his purifying material from ferrous sulfate, lime, and waste tanning bark that the essential details of our present iron oxide purification system became established. Laming spread out the mixture to oxidize in the air, and then filled it into boxes, on trays, through which the crude gas was made to pass. The fouled mass was taken out and regenerated by oxidation in the air. Few of the changes made in later years were of real

480 Proteus, *Gas World*, **100**, 447-52 (1934).
481 TerNedden, W., *Tech. Mitt. Krupp*, **4**, 8-9 (1936); *Chem. Abs.*, **30**, 7821 (1936).

importance, the outstanding ones, perhaps, being the replacement of the precipitated iron hydroxide by natural products such as bog iron ore, or industrial byproducts such as the iron hydrate sludges obtained in the manufacture of aluminum from bauxite. Regeneration of the used mass was later accomplished by the addition of enough oxygen or air to the gas to oxidize iron sulfide continuously, and a removal of the mass from the boxes was obviated. Laming's waste tanning bark, which had been added to loosen the mass and facilitate the passage of gas, was replaced by wood shavings, peat moss, coke breeze, infusorial earth, and other carriers. Metal salts of all kinds were added to increase the activity of the mass, but they never became of any importance. Finally, considerable attention was paid to mechanical details, such as the shaping of the mass in definite forms, e.g., balls or nodules, and the replacement of the boxes by towers, centrifuges, etc. These developments are considered in Chapter 26.

The mechanism of cyanogen removal in oxide boxes, though the subject of many studies, has never been cleared up satisfactorily. However, a few points have been brought out by these investigations which have served to improve the operation of oxide purifiers. Buhe [482] estab-

lished at a very early date what may well be axiomatic, namely, that hydrocyanic acid does not react with ferric compounds. He determined ferrous and ferric hydroxide in his fresh mass and, after several regenerations, found the very interesting values shown in Table XXVI. Buhe attributed the large amount of retained cyanogen to the high ferrous hydroxide content of his masses.

Feld [438] also was of the opinion that only ferrous oxide is capable of taking up cyanogen, as was Offe.[444] However, it is doubtful that it is actually oxide with which the cyanogen combines, for fresh mass in spite of its high content of ferrous hydroxide does not absorb any.[435, 444, 483] Drory's [450] opinion to the contrary is so much in the minority that it may be discounted. It is much more likely that ferrous sulfide is the active agent.[435, 478, 483, 484] Burschell and Poole are especially firm in this opinion. Burschell claimed that hydrogen cyanide was taken up by masses which no longer absorb hydrogen sulfide, and Poole stated that, on passage of an inert gas containing hydrogen cyanide through a thoroughly sulfided box, hydrogen sulfide appeared in the exit gas. Feld [438] thought that ferrous sulfide did not absorb hydrogen cyanide, or at least

482 Buhe, A., and Schilling, N. H., *J. Gasbeleucht.*, 11, 244–54 (1868).

483 Burschell, E., *ibid.*, 36, 7–10 (1893).
484 Poole, H., *J. Gas Lighting*, 70, 1234–6 (1897).

TABLE XXVI

Change in Composition of Oxide in Gas Purifiers Caused by Cyanogen Retention [482]

Compound	Fresh Mass percent	Used Once percent	Used Four Times percent	Used Eight Times percent
Ammonium ferrocyanide and ammonium cyanide	. . . . .	1.00	3.00	4.40
Ferric hydroxide	37.13	16.96	6.51	1.17
Ferrous hydroxide	20.71	24.86	20.39	15.65
Prussian blue	. . . . .	5.93	7.84	11.12
Ammonium thiocyanate	. . . . .	4.69	7.82	14.08

only slowly and by a secondary reaction involving oxygen. It is likely that he made his tests with old iron sulfide, which is rather inactive toward hydrogen cyanide. Knublauch [485] brought out this factor a number of decades before Feld's work, but it has been emphasized in more recent years by Gluud, Klempt, and Brodkorb [486] that only freshly prepared (amorphous) iron sulfide will react with hydrogen cyanide; aged (crystalline) material will not.

Be that as it may, the effect is that ferrous cyanide is formed by either one or both of the following equations:

$$Fe(OH)_2 + 2HCN \rightarrow Fe(CN)_2 + 2H_2O$$

$$FeS + 2HCN \rightarrow Fe(CN)_2 + H_2S$$
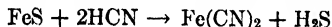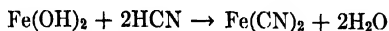
The ferrous cyanide thus formed probably associates to form $Fe_2Fe(CN)_6$, Prussian white, which is easily oxidized by air to form Prussian blue, $Fe_7(CN)_{18}$. It is also possible that the ferric oxide contained in the mass reacts with the Prussian white to give the blue form, for Gluud and Jacobson [12] have stated that both the blue and the white compounds are formed in dry boxes operated in the absence of air. The overall equation for these reactions is usually written thus:

$$4Fe(OH)_3 + 3Fe(OH)_2 + 18HCN \rightarrow$$
$$Fe_7(CN)_{18} + 18H_2O$$
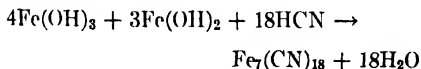
but it is doubtless a sum equation, since reactions of such high order are not readily conceivable.

An outgrowth of the realization that ferrous compounds are necessary for good cyanogen absorption may be seen in some modern practices. Offe [444] never used fresh mass exclusively when starting new boxes.

He mixed fresh mass with regenerated mass in the ratio of 3 : 1 and thus achieved a cyanogen removal of 99 to 99.5 percent and also much higher blue content than normal. Kaudela [487] never mixed old and new mass, but preferred to give new purifying material an initial treatment with raw gas, followed by regeneration, before using it in the final box. However, he did not seem to obtain the excellent removal reported by Offe.

Residual ammonia (pyridine, etc.) in the gas plays an important role in the operation of the dry boxes. It both favors conversion of the iron oxides to ferrous sulfide and takes an active part in the cyanogen absorption. As a matter of fact, spent oxide contains not only Prussian blue but also one or several ammonia-iron complex cyanides. Bunte [488] pointed this out at an early date and tried to get to the root of it by determining the ratio of ammonia to cyanogen. The lack of differentiating analytical methods made his task impossible of fulfillment. Knowledge gained in investigations of liquid cyanogen-recovery systems [437, 438] allows the assumption that ferrous cyanide combines with ammonium cyanide to form complex compounds such as $(NH_4)_4Fe(CN)_6$ and $(NH_4)_2FeFe(CN)_6$. These can then give rise to the formation of other iron-ammonia-cyanogen compounds in which the iron may be partly in the ferrous and partly in the ferric state. In any event, the presence of ammonia in the gas facilitates the absorption of hydrogen cyanide by the oxide masses, according to Bertelsmann; [441] and for this reason it is perhaps fortunate that some ammonia (pyridine, etc.) always gets by the ammonia saturators. In many

[485] Knublauch, O., *Dinglers Polytech. J.*, **267**, 323 (1888) ; *J. Gasbeleucht.*, **31**, 374–5 (1888).
[486] Gluud, W., Klempt, W., and Brodkorb, F., *Ber. Ges. Kohlentech.*, **4**, 51–72 (1932).

[487] Kaudela, E., *Gas- u. Wasserfach*, **73**, 110–2 (1930).
[488] Bunte, H., *J. Gasbeleucht.*, **31**, 542–4 (1888).

plants a certain amount is left in the gas intentionally. Murphy [474] thought that the upper limit should be 6 grains per 100 cubic feet.

However, this practice should not be overdone, because a large amount of ammonia or strong fixed alkali in the oxide boxes gives rise to the formation of thiocyanates, which are undesired in working up the "blue" content of the spent oxides and lessen correspondingly fixation of cyanogen as "blue." Bunte [488] first warned against it, and Leybold [435] also brought out its undesirability. Burschell [488] postulated that thiocyanate formation occurs in the fouling stage as well as in the regeneration. Nothing can be done about formation in the fouling stage, but formation in the regeneration can be cut down materially if the mass is spread out and kept moist during regeneration, in order to avoid heating. He observed, incidentally, that though ammonia promotes the formation of thiocyanate, it does not do so to the exclusion of "blue" production. Knublauch [80] agreed completely with Leybold and Burschell and tabulated a large number of analyses of spent oxides in support of his argument. In one analysis, the amount of thiocyanate was three times that of complex iron cyanides. Poole [484] also pointed out that ammonia in the gas should be kept low to avoid the conversion of cyanogen to thiocyanate, for which reaction the ideal conditions are given in the oxide box: the simultaneous presence of hydrogen sulfide, sulfur, and ammonia. Other investigators who have called attention to this problem are Lewis,[478] Leybold in a later paper,[489] and especially Feld.[438, 490] Feld probably overshot the mark when he asserted that a high ammonia content of

spent oxide also denotes a high thiocyanate content; for, though his table of analyses seems to prove his point, other analyses offered by Bueb [445] certainly refute this assertion. However, the Bueb analyses are no argument against the validity of the general doctrine that ammonia promotes thiocyanate formation under the conditions of the oxide box.

Where the removal of cyanogen from the gas is of paramount importance, or where thiocyanates are desired rather than Prussian blue, ammonia may be added to the gas in larger amounts. In the Williams process,[82] oxide with at least 50 percent sulfur is kept very moist by spraying, and the gas is passed through. The cyanogen is fixed as thiocyanate, which dissolves in the descending liquor. An efficiency of 95 to 98 percent is reached. Downing [468] left enough ammonia in the gas to take care of a cyanogen content of 20 grains per 100 cubic feet and thus obtained a complete removal.

Because of the comparative slowness of the reactions involving complex iron cyanides, it has often been urged that oxide boxes be made amply big so that the gas current will be correspondingly slow. In this fashion a high "blue" content of the spent mass has been said to be assured. Exponents of this school of thought were especially Leybold [435, 489] and Feld.[438] Bertelsmann [441] did not think much of this idea.

Additional papers on the general subject of oxide purification recommended for study are those of Feld,[491] Clayton, Williams, and Avery,[492] Geipert,[493] Brück-

[489] Leybold, W., *ibid.*, 40, 774–6, 789–91, 803–5 (1897).

[490] Feld, W., *ibid.*, 46, 228–9 (1903).

[491] Feld, W., *ibid.*, 46, 561-7, 603 6, 629 32, 642–5, 660–6 (1903).

[492] Clayton, R. H., Williams, H. E., and Avery, H. B., *Gas J.*, 196, 311–5 (1931) ; *Gas World*, 95, 371–3 (1931).

[493] Geipert, R., *Gas- u. Wasserfach*, 71, 76–9

ner,[493] and Thau.[493] The last paper deals with the subject of purification under high pressures.

When the oxide masses have reached a sulfur content of about 30 to 50 percent they are discarded and sometimes worked up for their cyanide content or used in the manufacture of sulfuric acid. A very complete analysis of such a spent oxide was given by Williams [417] and is reproduced in Table XXVII. The complexity of this ma-

TABLE XXVII

AN ANALYSIS OF SPENT OXIDE [417]

	Percent
Free sulfur	44.70
Moisture	17.88
Ferric monohydrate	5.26
Ferrous monohydrate	6.25
Basic ferric sulfate	1.25
Ferric ammonium ferrocyanide	3.80
Ferrosoferric ammonium ferrocyanide	2.50
Ferric pyridic ferrocyanide	1.20
Organic matter peat fiber	4.68
Tar	1.21
Silica	1.05
Naphthalene	0.72
Pyridine sulfate	0.77
Ammonium sulfate	2.06
Calcium sulfate	0.12
Ferrous sulfate	0.02
Ammonium thiocyanate	1.30
Sulfur otherwise combined	1.33
Organic matter soluble in alkalies (humus)	1.54
Combined water and loss (by difference)	2.36
	100.00

terial proves a great handicap to its proper utilization, and as a result innumerable schemes have been proposed for the recovery of its cyanide and sulfur content. In general, they fall into two main groups:

(1928). Brückner, H., *ibid.*, **81**, 882–8 (1938). Thau, A., *Gas World*, **109**, No. 2826, Coking Sect., 115–8 (1938).

those which remove the sulfur first and then the cyanides, and those which recover the cyanides first and leave the sulfur behind. The first group offers the better conditions for a total recovery of all values, but it is feasible only if sulfur prices are sufficiently high and if plants are sufficiently large to warrant the costly equipment necessary for the handling and recovery of a highly inflammable solvent. Carbon bisulfide still is the best solvent for the purpose, in spite of the ardent search for cheaper and less dangerous liquids of sufficiently high solvent power for sulfur.

The reasons for the desirability of first removing the sulfur from the mass are very simple. Conversion of the insoluble complex iron cyanides of the spent oxide to water-soluble ferrocyanides (prussiates) requires the action of strong alkalies. Under these conditions, however, sizable amounts of the available "blue" are transformed to thiocyanates, which do not have much of a market and are therefore not usually wanted. Furthermore, the hauling of ballast sulfur from the point of production of the mass to the chemical processing plant piles unnecessary freight charges on the end products, and the dragging of the sulfur through the various stages of prussiate manufacture is cumbersome and uneconomical.

In spite of these good reasons for an initial removal of the sulfur, the larger quantity of spent oxides is worked up by processes of the second group which are a compromise between the desirable and the economically tolerable. They leave the sulfur in the mass, and they use alkali of such strength and in such manner that only a small amount of the "blue" is converted to thiocyanate.

The process of Kunheim and Zimmer-

mann,[494] which, according to Köhler,[495] is based on the ideas of Gautier and Bouchard, is typical. The spent oxide is first treated with water in order to dissolve the soluble ammonia salts and the thiocyanates. For this purpose the mass is lixiviated systematically in wooden filter vats, the water being left in each vessel for 12 hours, and the liquor being pumped from one to another. The final solution, containing 30 to 40 grams of ammonia per liter, is distilled with lime to release its ammonia content; the resultant calcium thiocyanate usually goes to waste. After superficial air drying, the mass is mixed with an amount of hydrated lime corresponding to the "blue" content found by analysis and brought into the filter vats for extraction with water. The lime decomposes the complex iron cyanides with formation of calcium ferrocyanide, and the final liquor contains the equivalent of about 120 to 140 grams per liter potassium ferrocyanide, with small amounts of calcium thiocyanate, gypsum, and tarry and other organic matter. In order to prepare pure prussiate from such impure liquor, its calcium ferrocyanide content is precipitated in the form of rather insoluble double cyanides such as calcium-potassium ferrocyanide, from which pure potassium ferrocyanide is then made by double decomposition with potassium carbonate.

Those readers who desire further details about the many processes in existence for working up spent oxide masses are referred to the excellent books by Williams,[417] Bertelsmann,[441] Köhler,[495] and Bössner.[496]

Several papers and patents have been published since these books appeared in print.[418, 497]

DIRECT RECOVERY OF CYANOGEN

Although for many years the oxide box was the only means of recovering cyanogen from gas, the difficulties encountered and the incompleteness of removal brought about efforts to abstract it from the gas in more direct fashion. As has been pointed out above, only a little cyanogen remains in the ammonia liquor, the larger portion going on with the gas. Since the total available amount is very small to begin with, its recovery from ammonia liquor, though often attempted, has never become successful. Methods proposed aim at recovery either as thiocyanates or as ferrocyanides, and, owing to the low concentration of the cyanogen compounds in the ammonia (still) liquors, recovery must be made as an insoluble compound.

According to Spence,[498] waste from the ammonia stills has been precipitated with a mixture of ferrous sulfate and copper sulfate, producing a precipitate of insoluble cuprous thiocyanate which will react with ammonium sulfide to furnish ammonium thiocyanate. Storck and Strobel[499] also made cuprous thiocyanate, but they produced it directly from gas liquor, which they acidified and precipitated with cupric chloride and sodium bisulfite. Parker and

[494] Kunheim, H., and Zimmermann, H., Ger. Pat. 26,884 (1883).

[495] Köhler, H., *Die Industrie der Cyanverbindungen*, F. Vieweg, Braunschweig, 1914, 200 pp.

[496] Bössner, F., *Die Verwertung der ausgebrauchten Gasreinigungsmassen auf Blutlaugensalz, Ammoniak und Rhodanverbindungen*, F. Deuticke, Vienna, 1902, 93 pp.

[497] Anon., *Gas World*, **57**, 497 (1912). Anderson, W., Brit. Pat. 127,128 (1918). Grube, G., and Dulk, B., *Z. angew. Chem.*, **33**, 141–4 (1920). Szombathy, K., Ger. Pat. 488,417 (1927). Broche, H., Nedelmann, H., and Thomas, H., *Brennstoff-Chem.*, **13**, 201–9 (1932). Bertrand, M. F., Brit. Pat. 462,934 (1937).

[498] Spence, P., *Chem. News*, **18**, 119 (1868).

[499] Storck, F., and Strobel, C. H., *Dinglers Polytech. J.*, **235**, 156 (1880). Lunge-Köhler, Vol. 2, p. 421, of ref. 4.

Robinson [500] conceived the method which even today is the best for preparing cuprous thiocyanate: precipitation with cupric sulfate and sulfur dioxide. Bower [501] used cuprous chloride and precipitated from still waste a mixture of cuprous thiocyanate and copper ferrocyanide. Schönfeld, [502] in more modern times, treated gas liquors with sulfur or sulfides in the presence of active carbon to convert their cyanogen content to thiocyanates, which he recovered by distillation.

Grossmann [503] based his proposal for making ferrocyanides from ammonia liquor on the supposed fact that, when fresh, it contains only ammonium cyanide. He added a large excess of ferrous sulfide and ammonium sulfide, allowed the mixture to settle, distilled the liquor in the ammonia still in normal fashion, and precipitated the calcium ferrocyanide contained in the still waste as Prussian blue or as insoluble ferrous ferrocyanide. Basore [504] advocated a hybrid scheme, according to which still waste was first treated with iron salts to remove ferrocyanides as insoluble ferrous ferro compounds, and then treated with ferrous sulfate and cupric sulfate to remove the thiocyanates as the insoluble copper salt. None of these process is of any commercial importance.

The main emphasis of investigators in the field of cyanogen recovery has properly been placed on the gaseous phase. A very natural thought was simply to treat the gas with an alkali. However, the very large preponderance of carbon dioxide and hydrogen sulfide, and their greater acidity, make this next to impossible. Lime, as milk of lime, has been proposed on account of its cheapness, [505] but it is difficult to see how it could be used in practice, except with an excessive loss of lime as calcium carbonate. This was probably realized by Taplay, [457, 506] who proposed the use of chalk instead, and asserted that 1 ton would clean 11 million cubic feet of gas. Broadhead [507] noted the purifying effect of calcium carbonate in a calcium chloride gas-dehydration plant, finding the cyanogen content reduced from 21 to 5 grains per 100 cubic feet. In view of the fact that calcium cyanide in aqueous solution is hydrolyzed to a very large extent, it seems surprising that lime or chalk treatment has achieved any success at all. This reaction may be attributed to iron oxide or carbonate contained in the lime, which would be expected to combine with the cyanogen to form complex calcium ferrocyanide. These doubts are perhaps borne out by the findings of Liebknecht, [508] who stated that, when gas containing ammonia, carbon dioxide, and hydrogen cyanide is scrubbed with solutions of alkaline-earth salts, the cyanogen is not absorbed at all but passes on with the gas and may be recovered by a caustic wash in a separate step.

Another treatment of gas with lime came to the attention of the author of this chapter through several German patents laid out for public inspection, which have not issued. The proposal is at least of theo-

[500] Parker, T., and Robinson, A. E., Brit. Pat. 2,383 (1890). Lunge-Köhler, Vol. 2, p. 421, of ref. 4.

[501] Bower, H., Ger. Pat. 88,052 (1896); Brit. Pat. 361 (1896); Lunge-Köhler, Vol. 2, p. 421, of ref. 4.

[502] Schönfeld, F., Fr. Pat. 638,035 (1927).

[503] Grossmann, J., Brit. Pat. 19,988 (1907); J. Soc. Chem. Ind., 27, 393 (1908).

[504] Basore, C. A., U. S. Pat. 1,323,239 (1919).

[505] McArthur, W., U. S. Pat. 933,097 (1909). Cisélet, E., and Deguide, C., Ital. Pat. 494,211 (1919).

[506] Taplay, J. G., Gas J., 155, 589–90 (1921); Gas World, 75, 234 (1921). Taplay, J. G., and Galbraith, W. L., Brit. Pat. 220,024 (1922).

[507] Broadhead, C. F., Gas J., 217, 217–8 (1937).

[508] Liebknecht, O., U. S. Pat. 1,606,767 (1926).

retical interest and deserves credit for being novel. It contemplates passing the hot gases, above 600° C, over lime, magnesia, etc., forming calcium cyanide and from that calcium cyanamide, as expressed by the following equations:

$$CaO + 2HCN \rightarrow Ca(CN)_2 + H_2O$$

$$Ca(CN)_2 \rightarrow CaNCN + C$$
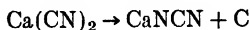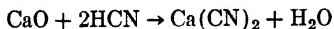
It has been advocated repeatedly that caustic alkalies, such as sodium hydroxide,[509, 510] be used, but this suggestion could hardly be of any practical importance. The use of ammonia, however, has at least the advantage of making the gas furnish its own alkali. According to O'Neill,[511] it is possible to remove all the hydrogen cyanide from gas by washing it with an ammonia liquor under specified conditions. Davidson[512] worked along the same lines, and Perna[513] determined the best operating conditions. There seems little doubt that, by proper dephlegmation of such ammoniacal liquors in the ammonia still, gases comparatively rich in hydrogen cyanide could be obtained. A combination treatment with lime slurried in ammonia liquor was offered by Cisélet and Deguide.[514]

By far the largest number of processes for the recovery of cyanogen from coal-distillation gases is based on the readiness of iron to form numerous complex compounds with cyanogen. This property has already been referred to above in connection with iron oxide purification, for which it is the basis. It is not surprising that people tried to utilize the reactions of the oxide box in a manner which allowed them a better control and moreover gave them better products. The primary aim was to produce directly the soluble ferrocyanides usually obtained only by tediously working up spent oxides. Ortlieb and Müller, as reported by Willm,[515] were probably the first to use suspensions of iron oxides to remove hydrogen cyanide from a gas. They precipitated ferrous chloride with milk of lime and scrubbed with this slurry a gas made by thermal decomposition of methylamines, and containing considerable quantities of hydrogen cyanide. Knublauch[485, 516] applied this principle to the gas industry, proposing as active agents the oxides, hydrates, carbonates, or sulfides of alkalies, alkaline earths, and ammonia in mixtures with the oxides, hydroxides, or carbonates of iron, manganese, or zinc. He stated that, if the components of either group were in excess, insoluble iron-complexes might precipitate. In practice the only components used were ferrous sulfate and sodium carbonate. Knublauch's process was not so successful as it deserved to be, perhaps because the industry was not ripe for it, perhaps because it was somewhat burdened by the fact that it did not make soluble salts to the exclusion of insoluble compounds. The insolubles ran as high as 20 percent of the total cyanogen. Feld,[438] in a beautiful study, pointed out that the insolubles were due to an admixture of ferric hydroxide, which is invariably

509 Raupp, H., and Thilo, J., Ger. Pat. 230,502 (1910). Garner, J. B., Miller, R. W., and Shaner, G. A., U. S. Pat. 1,609,872 (1926). Garner, J. B., and Shaner, G. A., Can. Pat. 270,011 (1927). Claude, G., U. S. Pat. 1,717,761 (1929).

510 Heffner, L. W., and Tiddy, W., U. S. Pat. 1,600,228 (1926).

511 O'Neill, J. G., *Progressive Age*, **30**, 868–9 (1912) ; *J. Gasbeleucht.*, **56**, 304 (1913).

512 Davidson, W. B., Brit. Pat. 23,696 (1912) ; *Gas World*, **58**, 7 (1913).

513 Perna, F., *Plyn a voda*, **9**, 181 (1929) ; *Paliva a Topent*, **11**, 158 (1929) ; *Chem. Abs.*, **24**, 5977 (1930).

514 Cisélet, E., and Deguide, C., U. S. Pat. 1,349,750 (1920).

515 Willm, E., *Bull. soc. chim.*, (2), **41**, 449–51 (1884).

516 Knublauch, O., Brit. Pat. 15,164 (1887).

formed when batches of ferrous hydroxide are made for storage. He advised adding the ferrous salt and the alkali to the scrubbers as needed. When air was carefully excluded Feld was able to convert the hydrogen cyanide to soluble ferrocyanide to the extent of 98.8 percent. He also blamed a deficiency of alkali for the formation of insolubles, a ratio of three moles of carbonate to one mole of iron sulfate being necessary for good operation. From the large number of equations given for the Knublauch process by Feld only these may be cited:

$$Fe(OH)_2 + 2Na_2CO_3 + 6HCN \rightarrow$$
$$Na_4Fe(CN)_6 + 4H_2O + 2CO_2$$

(absence of air)

$$4Fe(OH)_2 + 2Fe_2(OH)_6 + 2Na_2CO_3$$
$$+ 24HCN \rightarrow$$
$$Fe_7(CN)_{18} + Na_4Fe(CN)_6 + 2CO_2 + 22H_2O$$
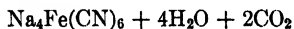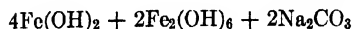
(presence of air)

Strangely, Feld was of the opinion that the Knublauch process should be carried out after ammonia removal in order to avoid the formation of thiocyanate, an idea also brought forth by Leybold.[135] This opinion was thoroughly disproved by later investigators, though it is found again and again in papers and patents.

Knublauch's contemporary Rowland[517] removed cyanogen from gas by using its ammonia content as an alkali. He added soluble iron salts to the ammonia scrubbers, thus forming soluble ammonium ferrocyanide. Further addition of iron salt, just before distillation of the liquor, precipitated insoluble ammonium ferroferrocyanide. With this step, the Rowland process became in a way the forerunner of the

Bueb process, which will be discussed below. An almost identical scheme was proposed by Wilton.[518]

Foulis[519] enlarged on the Knublauch process and deserves credit for having made a success of it. He precipitated ferrous chloride solution with sodium or potassium carbonate, slurried the resulting mixture of ferrous hydroxide and ferrous carbonate in more alkali carbonate solution, and scrubbed the gas with this slurry. The process was installed after ammonia removal, and Foulis insisted that this was essential. A special scrubber for the handling of the slurries involved, invented by him and Holmes,[520] was widely adopted and imitated. A diagram of the Holmes washer is shown in Fig. 11.[521] The Foulis process was discussed from a theoretical standpoint by Feld,[438] and was briefly described by Hunt.[522] An identical process was conceived independently by Lewis,[478] who gave his recovery as 3 to 4.5 pounds of sodium ferrocyanide per ton of coal carbonized, and a similar scrubber has been described by Lewis and Cripps.[523] Farmer and Somerville[524] worked along the same line, but placed the process before the ammonia scrubbers; they seemingly used a deficient amount of soda ash. Tillinghast[525] received a patent on a special ratio of iron carbonate to sodium carbonate.

The Knublauch-Foulis process had a very thorough trial by Jorissen and Rut-

517 Rowland, W. L., U. S. Pat. 465,600 (1891).

518 Wilton. J. Gasbeleucht., 37, 108 (1894).
519 Foulis, W., Brit. Pat. 9,474 (1893) ; J. Gas Lighting, 69, 1053-4 (1897).
520 Foulis, W., and Holmes, P., Brit. Pat. 15,168 (1896).
521 Bertelsmann, W., p. 226 of ref. 441.
522 Hunt, C., J. Gasbeleucht., 40, 18-9 (1897).
523 Lewis, G. P., and Cripps, R. A., Brit. Pat. 20,883 (1896).
524 Farmer, W. J., and Somerville, J. M., Brit. Pat. 4,410 (1899).
525 Tillinghast, A. R., U. S. Pat. 1,252,741 (1918).

ten,[489, 526] who reported that it worked very satisfactorily It was placed before the ammonia scrubbers and thus gave a 20 percent higher yield This increased yield was doubtless due to the fact that no cyanogen was diverted to the ammonia of Feld [488] They found between 15 and 33 percent of the precipitated mixture of ferrous carbonate and hydroxide to be oxidized to the ferric form, and they noted a considerable production of insolubles which they found to contain Prussian blue, am-
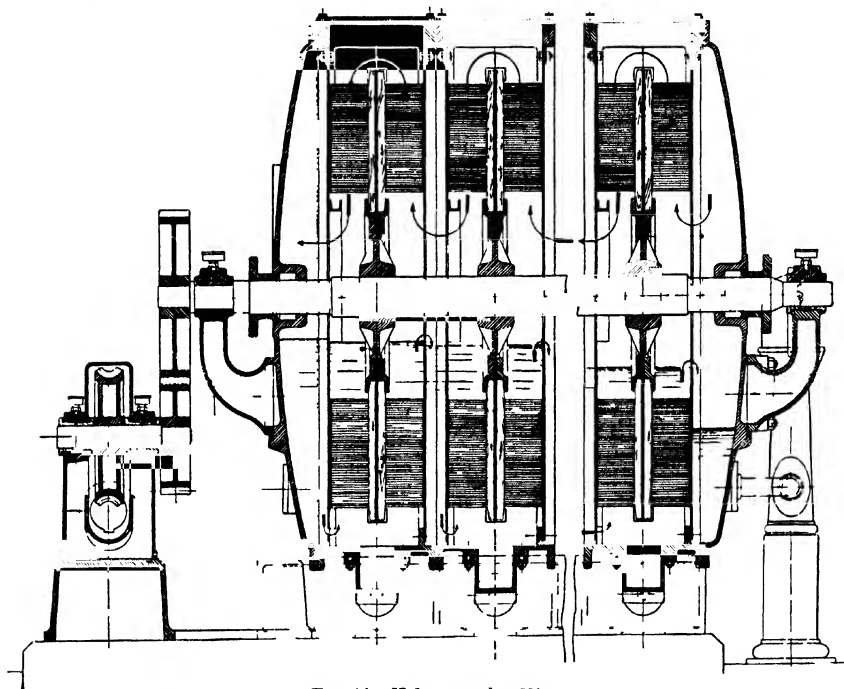
Fig 11   Holmes washer [521]

liquor In spite of the presence of ammonia there was no appreciable formation of thiocyanates, and this finding is of great importance in view of the contrary opinions expressed by many workers in the field, including Feld On the other hand, as far as the formation of insolubles is concerned, Jorissen and Rutten came to conclusions which are identical with those monium ferroferrocyanide, potassium ferroferrocyanide, and iron sulfide The mixture was decomposed with the aid of caustic potash to give more potassium ferrocyanide, which was added to the bulk of the product From time to time sodium sulfate was removed from the mother liquors, in which it slowly accumulated The authors gave considerable data on the interconversion of soluble and insoluble complex cyanides, and they speculated quite a

526 Rutten, J , Het Gas, 22, 182 (1902)   J
Gas Lighting, 80, 879 82 (1902)

bit on the reaction mechanism of the process. The consumption of raw materials per pound of potassium ferrocyanide was 2 pounds iron sulfate, 0.9 pound sodium carbonate, 0.67 pound potassium carbonate, and 0.45 pound potassium hydroxide.

A later description of the Knublauch process, erroneously ascribed to Rutten, was given anonymously.[527] The pattern of the operation was about the same, except that the ferrous sulfate was precipitated with ammonia liquor, the hydroxide slurried in sodium carbonate solution, and sodium ferrocyanide consequently produced. The insolubles were treated with soda ash and lime.

An interesting application of the Knublauch process has been made by Pieters,[472, 528] who fitted it into his hydrogen sulfide-removal process, in which he needed ferrocyanides. He treated the hot vapor coming from the ammonia still with solutions of sodium or potassium carbonate and ferrous sulfate (also metallic iron), thus forming the corresponding prussiates. The operating temperature was 95° C, and accordingly solutions of high concentrations, 500 to 600 grams per liter, were obtained.

Attempts to overcome the troubles caused by the impurities introduced in the step of precipitating the original iron sulfate were made by Coleman[529] and by Hempel.[529] Coleman proposed using native iron ores in alkaline suspension as the scrubbing agent; Hempel used finely divided metallic iron. Hempel's idea would seem particularly appropriate, since iron is so easily attacked by hydrogen sulfide as well as by hydrogen cyanide.

Since iron sulfide is invariably formed in the Knublauch process, Johnson[530] proposed to treat the original iron compound, e.g., sulfate, with an alkali ferrocyanide, thus producing what he thought to be ferrous cyanide (in reality probably an alkali ferroferrocyanide), which was then supposed to be used in alkaline suspension for the further cleaning of gas, and no iron sulfide was to be formed. This proposal is probably based on Feld's[531] finding that ammonium ferroferrocyanide behaves like any other ferrous compound, reacting with hydrogen cyanide and forming ammonium ferrocyanide:

$$(NH_4)_2FeFe(CN)_6 + 6NH_3 + 6HCN \rightarrow$$
$$2(NH_4)_4Fe(CN)_6$$
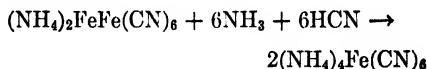
Tillinghast[532] also wanted to use sodium ferroferrocyanide for the absorption stage, but his purpose was not to avoid the formation of iron sulfide. He wanted to utilize mother liquors from the manufacture of crystallized sodium ferrocyanide and proposed to precipitate them with copperas solution, reintroducing the insoluble complex into the gas-scrubbing stage together with fresh iron carbonate. Espenhahn[533] cleverly combined this scheme with the well-known liberation of hydrogen cyanide from ferrocyanides with the aid of

527 Anon., *Boll. assoc. ital. ind. gaz acqua*, 1913, No. 4; *Ind. chim.*, 13, 340–1 (1913); *Chem. Abs.*, 8, 815 (1914).

528 Pieters, H. A. J., *Chem. Eng. Congr., World Power Conf.*, 1936, Advance proof No. C10, 12 pp.; *Chem. Abs.*, 31, 3240 (1937); *Brennstoff-Chem.*, 18, 373–6 (1937); Ger. Pats. 646,192 (1937), 676,936 (1939); U. S. Pat. 2,-169,282 (1939). Pieters, H. A. J., Penners, K., and Hovers, J., *Het Gas*, 57, 306–14 (1937). Directie van de Staatsmijnen in Limburg and C. Otto & Co. G.m.b.H., Fr. Pat. 882,955 (1938); Brit. Pat. 497,331 (1938); *Chem. Abs.*, 33, 3977 (1939).

529 Coleman, W. H., Brit. Pat. 27,908 (1912). Hempel, H., Ger. Pat. 404,428 (1923).

530 Johnson, J. Y., Brit. Pat. 5,775 (1906).

531 Feld, W., *J. Gasbeleucht.*, 47, 182–6, 157–9, 179–84 (1904).

532 Tillinghast, A. R., U. S. Pat. 1,252,742 (1918).

533 Espenhahn, E. V., U. S. Pat. 1,315,219 (1919); U. S. reissue 15,090 (1921); Brit. Pat. 109,254 (1917); Can. Pat. 189,364 (1919).

strong acids, in an effort to recover the cyanogen of the gas in its most valuable form, as hydrogen cyanide. He washed gas with a slurry of sodium ferroferrocyanide in concentrated sodium carbonate solution, whereby sodium ferrocyanide was formed:

$$Na_2FeFe(CN)_6 + Na_2CO_3 + H_2S \rightarrow$$
$$Na_4Fe(CN)_6 + FeS + H_2O + CO_2$$

$$FeS + 6HCN + 2Na_2CO_3 \rightarrow$$
$$Na_4Fe(CN)_6 + H_2S + 2CO_2 + 2H_2O$$
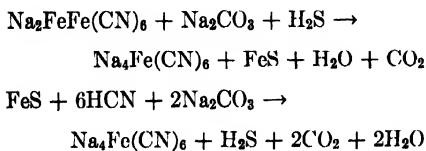
The solid sodium ferrocyanide obtained on crystallization was decomposed with sulfuric acid to yield hydrogen cyanide and insoluble ferroferrocyanide, which went back into the system

$$2Na_4Fe(CN)_6 + 3H_2SO_4 \rightarrow$$
$$Na_2FeFe(CN)_6 + 3Na_2SO_4 + 6HCN$$
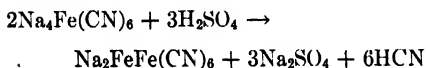
According to the inventor's paper on the subject [82] about 1 pound of hydrogen cyanide per ton of coal carbonized is recovered by his process. The paper gives a good survey of the economics of the cyanide industry in general and of the Espenhahn process in particular.

A very similar proposal was advanced by Sperr,[534] the only difference being the use of sodium bisulfate instead of sulfuric acid and the conversion of the byproduct sodium sulfate to sodium carbonate. A number of patents and a paper relating to the subject of the production of soluble ferrocyanides from distillation gases, but without special significance, are merely referred to here.[535]

In the foregoing processes the recovery of pure ferrocyanides from the technical liquors containing impurities such as sodium sulfate, sodium chloride, sodium carbonate, and others is a job requiring great care and a knowledge of solubility conditions. The following references should be of help. Petri [536] made the potassium salt by double decomposition of sodium ferrocyanide with potassium chloride, obtaining a yield of 96 percent. Conditions of temperature and concentration are specified in his patent. Boberg [537] started from a solution containing prussiate and carbonate, evaporated at 80° C until concentrated, and crystallized after cooling to 35° C. Dominik [538] contributed a splendid phase-equilibrium study on the system Na_2SO_4-$Na_4Fe(CN)_6$. The latter salt shows a minimum solubility at 32° C. Above this temperature pure prussiate can be obtained; crystals formed below it are contaminated with sulfate. In a later study,[539] the same author worked out diagrams for the system $K_4Fe(CN)_6$-$Na_4Fe(CN)_6$-KCl-$NaCl$, in water and in alcohol. The problem involved is the production of the potassium from the sodium salt. Farrow [540] determined the solubilities and densities of sodium, potassium, and calcium ferrocyanides. Naamlooze-Vennootschap Stikstof-

[534] Sperr, F. W., Jr., Can. Pat. 232,600 (1923); U. S. Pat. 1,524,113 (1925).

[535] Lessing, R., Brit. Pat. 2,090 (1907). Wright, W. H., U. S. Pat. 1,259,702 (1918). Dessemond, A., and Delclève, A. H., Brit. Pat. 181,719 (1922). Delclève, A., *Chimie & indus-*

trie, **10**, 632–5 (1923). Coulier, S., U. S. Pat. 1,604,565 (1926). Hamburger Gaswerke G.m. b.H., Fr. Pat. 692,868 (1930). Brandt, R., Brit. Pat. 349,692 (1930); U. S. Pat. 1,855,090 (1932).

[536] Petri, C., Ger. Pat. 212,698 (1907).

[537] Boberg, T., and Techno-Chemical Laboratories, Ltd., Brit. Pat. 108,692 (1916). Boberg, T., Can. Pat. 186,184 (1918). Techno-Chemical Laboratories, Norw. Pat. 29,543 (1919).

[538] Dominik, W., *Przemysl Chem.*, **6**, 317–27 (1922); *Chem. Abs.*, **18**, 1773 (1924).

[539] Dominik, W., *Przemysl Chem.*, **8**, 97–108 (1924); *Chem. Abs.*, **18**, 3558 (1924).

[540] Farrow, M., *J. Chem. Soc.*, **129**, 49–55 (1926).

bindingsindustrie [541] found that the solubility of sodium ferrocyanide in water is depressed very much by the addition of a mixture of sodium carbonate and hydroxide. This makes possible a rather high end temperature of the process of crystallization. Friend, Townsley, and Vallance [542] determined the solubility of $Na_4Fe(CN)_6$ in water between 0 and 104° C, and they compared their values with those previously reported in the literature. Fleisher and collaborators [543] made extensive equilibrium studies in the systems $Na_4Fe(CN)_6$-$NaCl$-Na_2CO_3-Na_2SO_4-H_2O, $Na_4Fe(CN)_6$-$NaCl$-H_2O, and $K_4Fe(CN)_6$-K_2CO_3-K_2SO_4-H_2O. They came to the interesting conclusion that the crystallization of $Na_4Fe(CN)_6$ is more complete from a ternary or quaternary system containing sodium chloride, and they advocated for this reason the use of ferrous chloride.

As has already been pointed out above, the great disadvantage of the Knublauch process and its various modifications is the fact that it does not produce soluble ferrocyanides exclusively. This necessitates working up two different products, which is inconvenient and costly. Feld [438] pointed out that with proper ratios of alkali and ferrous hydroxide and with exclusion of air the formation of insolubles could be prevented. However, air could not be excluded in the Knublauch-Foulis process, because oxidation was inevitable when the ferrous hydroxide was prepared separately. On the other hand, if ferrous sulfate and alkali carbonate were added directly to the scrubber the product was so badly con-

taminated by sodium sulfate that the recovery of a pure prussiate was jeopardized. Feld [438, 544] proposed to overcome these difficulties by using lime as the alkali; the iron sulfate could then be added directly to the scrubbers, since the calcium sulfate thus formed would precipitate and be eliminated by filtration. He found that even calcium carbonate reacts with hydrogen cyanide, though more slowly than the free base, so that the carbon dioxide of the gas does not interfere too much. His process was based on the equation:

$$FeSO_4 + 3Ca(OH)_2 + 6HCN \rightarrow$$
$$Ca_2Fe(CN)_6 + CaSO_4 + 6H_2O$$
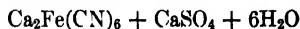
and did, indeed, produce only a soluble ferrocyanide. Inasmuch as calcium ferrocyanide lends itself ideally to the production of other prussiates by simple reactions with carbonates, it is probably better suited to the needs of the gas industry than any other salt.

In a later modification of his process Feld [545] tried to avoid the formation of iron sulfide by first precipitating iron sulfate with calcium ferrocyanide and using the insoluble iron-cyanogen complex as the scrubbing agent:

$$2FeSO_4 + Ca_2Fe(CN)_6 \rightarrow$$
$$3Fe(CN)_2 + 2CaSO_4$$
$$3Fe(CN)_2 + 6Ca(OH)_2 + 12HCN \rightarrow$$
$$3Ca_2Fe(CN)_6 + 12H_2O$$
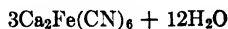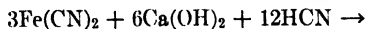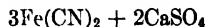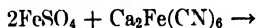
This modification eliminates dragging gypsum through the whole process, a distinct technical advantage. It is doubtless the basis for the proposal of Johnson,[530] to which reference has already been made, if indeed it is not identical with it.

[541] Naamlooze-Vennootschap Stikstofbindingsindustrie "Nederland," Dutch Pat. 13,904 (1925).
[542] Friend, J. A. N., Townsley, J. E., and Vallance, R. H., J. Chem. Soc., 1929, 2326–30.
[543] Fleisher, N. A., and Osokoreva, N. A., Trans. State Inst. Applied Chem. (U.S.S.R.), No. 26, 23–38, 38–47 (1935). Fleisher, N. A., and Plaksina, E. F., ibid., No. 26, 48–51 (1935); Chem. Abs., 29, 8246 (1935).

[544] Feld, W., Ger. Pat. 144,210 (1902).
[545] Feld, W., Ger. Pat. 178,635 (1905); Fr. Pat. 365,410 (1906); U. S. Pat. 832,466 (1906).

Feld's calcium ferrocyanide process was tried out in a German gas plant with genuine success, having been in continuous operation with only minor changes. A short description of it was given by Wolffram,[546] and an elaborate one by Stief.[546] These authors reported the cyanogen removal to be 95 and 80 percent, respectively.

A further modification of his process, which, however, never became successful, was suggested by Feld in a paper[531] and several patents.[547] It was inspired by his efforts to prevent thiocyanate formation in cyanogen-recovery processes working on gas containing ammonia. He planned to counteract the ammonia by having present in his scrubbing liquors salts capable of binding excess ammonia, as expressed in the following equations:

$$FeSO_4 + 8CaCl_2 + 6HCN + 16NH_3$$
$$+ 6CO_2 \rightarrow$$
$$Ca_2Fe(CN)_6 + 16NH_4Cl + 6CaCO_3$$
$$2MgCl_2 + 4NH_3 + 2CO_2 + 2H_2O \rightarrow$$
$$2MgCO_3 + 4NH_4Cl$$
$$2MgCO_3 + Fe(OH)_2 + 6HCN \rightarrow$$
$$Mg_2Fe(CN)_6 + 2CO_2 + 4H_2O$$
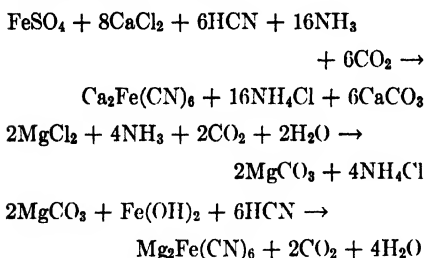
Since this suggestion represents a sort of Solvay ammonia-soda process, a proper ratio of ammonia and carbon dioxide is necessary and must be maintained, e.g., by addition of ammonia from the stills. According to Bertelsmann,[441] Feld even extended the process to the utilization of sodium sulfate, using a solution of Glauber's salt and copperas as a scrubbing agent, and making ammonium sulfate and sodium ferrocyanide.

In another modification, Feld[548] sought to remove cyanogen and ammonia from the gas simultaneously by scrubbing it with solutions or suspensions of such salts—e.g., alkalies, alkaline earths—as will form with ammonium salts double compounds of the ferrocyanide type. One such compound is $Ca(NH_4)_2Fe(CN)_6$. In other words, Feld purposely made the insolubles so carefully avoided in the Knublauch-Foulis process, and with this process actually approached Bueb's idea, which will be presented below in detail.

The problem of making calcium ferrocyanide from coke-oven gas remained dormant for several decades, probably on account of the high carbon dioxide content of the gas, which always causes loss of lime by conversion to calcium carbonate. More recently, however, it has been taken up again by Schreiber,[549] who utilized the final cooler water rather than the gas itself. Schreiber washed the gas with cold water, after ammonia removal, which absorbs all the hydrogen cyanide. The aqueous solution was blown with a circulating quantity of purified gas or air, from which the hydrogen cyanide was abstracted by means of lime and ferrous sulfate. When air was used, the ferrous sulfate was added to the dilute solution of calcium cyanide in a separate step, out of contact with the air, in order to prevent thiocyanate formation and oxidation to ferric compounds. The Schreiber process cleverly utilizes the high solubility of hydrogen cyanide in water in a way particularly suitable to coke-oven practice and has been in large-scale use. Two patents belonging in this group, but adding nothing of real value, are merely referred to here.[550]

[546] Wolffram, H., *Z. angew. Chem.*, **24**, 513-4 (1911). Stief, F., *Gas- u. Wasserfach*, **83**, 49-52 (1940).

[547] Feld, W., Ger. Pats. 151,820 (1902), 162,-419 (1904).

[548] Feld, W., Ger. Pat. 214,662 (1907).

[549] Schreiber, F. D., U. S. Pats. 2,110,244, 2,113,002 (1938).

[550] Ciselet, E., and Deguide, C., Brit. Pat. 9,780 (1915). Hood, J. J., Brit. Pat. 144,898 (1919).

To those who must deal with the problem of calcium ferrocyanide and its conversion to other prussiates, two recent references may be of interest. Farrow [540] has given its solubility in water from 24.9 to 99.7° C, and de Mesmacker [551] has discussed its conversion to sodium and potassium ferrocyanide with the aid of sylvinite.

While Feld had attempted to overcome the problem of insolubles in the Knublauch-Foulis process by adjusting its operation in such a fashion that they could not be formed, his contemporary Bueb [552] used the opposite approach and strove to make them, to the exclusion of soluble prussiates. At the same time Bueb wanted to use the alkali contained in the gas itself: ammonia. Since the insolubles were to be filtered off, contaminating soluble salts, unlike the sodium sulfate in the Foulis process, could be eliminated without difficulty.

Bueb's process contemplated washing the gas, before the ammonia was removed from it, with a strong ferrous sulfate solution under such conditions that an excess of ferrous compounds was maintained at all times. In the beginning, the copperas was converted to iron sulfide

$$FeSO_4 + 2NH_3 + H_2S \rightarrow$$
$$FeS + (NH_4)_2SO_4$$
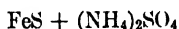
which reacted with the hydrocyanic acid of the gas, forming ferrous cyanide and ammonium ferroferrocyanide:

$$FeS + 2NH_3 + 2HCN \rightarrow$$
$$Fe(CN)_2 + (NH_4)_2S$$

$$2FeS + 6NH_3 + 6HCN \rightarrow$$
$$(NH_4)_2FeFe(CN)_6 + 2(NH_4)_2S$$
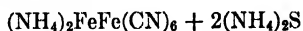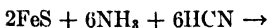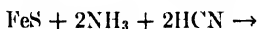
At this point the Bueb process really has come to an end, for, if the reaction mixture is left any longer in the scrubber, the gas will act on it with the formation of iron sulfide and soluble ammonium ferrocyanide:

$$Fe(CN)_2 + 4NH_3 + 4HCN \rightarrow$$
$$(NH_4)_4Fe(CN)_6$$

$$(NH_4)_2FeFe(CN)_2 + 6NH_3 + 6HCN \rightarrow$$
$$2(NH_4)_4Fe(CN)_6$$

$$(NH_4)_2FeFe(CN)_6 + 2NH_3 + H_2S \rightarrow$$
$$(NH_4)_4Fe(CN)_6 + FeS$$
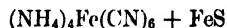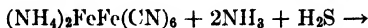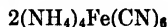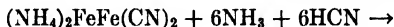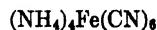
However, as in practice it is next to impossible to avoid entirely the formation of soluble prussiate, the final sludge was boiled, according to Bueb's original ideas, and the above reaction is reversed.

The mechanism of the Bueb process was investigated most thoroughly by Feld,[490, 551] to whom we owe a great deal for his painstaking work, even if some of his theories have proved to be untenable. He analyzed mud from various sections of the Bueb washer and thus followed the gradual conversion of iron sulfide via the insoluble iron-ammonium-cyanogen complexes to the end product, the soluble ammonium ferrocyanide. The final mud he found to contain about equal amounts of soluble and insoluble · compounds. Concerning Bueb's suggestion of insolubilizing the mud by boiling, Feld ascertained that such a procedure was ineffective, since some soluble material always remained in the ammonium sulfate liquor. This gave rise to trouble from discoloration when it was made into solid sulfate, as Rutten [526] also had occasion to find out. Moreover, boiling of the mud caused considerable loss of hydrogen cyanide, and Feld therefore advocated adding ferrous sulfate or sulfuric acid:

$$(NH_4)_4Fe(CN)_6 + FeS + H_2SO_4 \rightarrow$$
$$(NH_4)_2FeFe(CN)_6 + (NH_4)_2SO_4 + H_2S$$
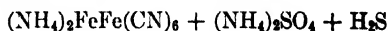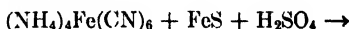
551 De Mesmacker, A., Fr. Pat. 726,425 (1931).
552 Bueb, J., Ger. Pat. 112,459 (1898). Brit. Pat. 9,075 (1899).

$(NH_4)_4Fe(CN)_6 + FeSO_4 \rightarrow$

$(NH_4)_2FeFe(CN)_6 + (NH_4)_2SO_4$
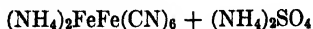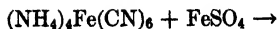
He contended that by properly adjusting the conditions of mud treatment it is even possible to eliminate completely the ammonia from the solid phase and to produce only $Fe_2Fe(CN)_6$. To obtain a better utilization of the iron, Feld suggested working as much as possible toward the soluble ammonium ferrocyanide by using more dilute ferrous sulfate solutions and by leaving the slurry in the washers for a long time. However, this would defeat the very purpose of the Bueb proposal.

Feld's fear that under the conditions of the Bueb process a lot of thiocyanate would be formed proved unfounded in practice. It is safe to say that, as long as oxygen is kept out of the gas, thiocyanate formation will be negligible.

Nauss [437, 553] also investigated the Bueb process, chiefly from the standpoint of the relative quantities of cyanogen and ammonia, and agreed in general with Feld's ideas. Keppeler [476] also considered $(NH_4)_2$-$FeFe(CN)_6$ to be the main constituent of blue mud, and his conceptions of the reaction mechanism are in line with those of Feld. He found the mud to contain from 10 to 35 percent of solubles. Hand [554] and Ost and Kirschten,[555] however, came to different conclusions. On the strength of an analytical study of many finished muds —in particular of their cyanogen-ammonia ratio—they postulated that the major component is a double salt $(NH_4)_2Fe(CN)_4$. A general consideration of the chemistry of complex iron-cyanogen compounds makes the existence of this compound highly doubtful. As to the quantities of soluble and insoluble materials in the muds, Hand considered a ratio of 1 : 2 a normal one. Guillet [556] is another author who studied the Bueb process. Bueb, from whom illumination on his own process should have come, unfortunately remained silent. Instead, he engaged in a fruitless polemic with Feld on points of minor importance.[445]

The actual operation of the Bueb process is usually carried out in a special horizontal scrubber, designed to handle thick slurries. It is based on the principle of the Holmes washer and is shown diagrammatically in Fig. 12.

According to Bueb,[445] a concentrated copperas solution (28 percent) is charged to the last section of the scrubber, i.e., countercurrent to the gas flow. The gas, which is here devoid of hydrogen cyanide but still contains ammonia and hydrogen sulfide, precipitates iron sulfide and forms ammonium sulfate. In the next section the iron sulfide is decomposed by the hydrogen cyanide, with liberation of hydrogen sulfide, and formation of the ammonium-iron-cyanogen complexes. The first section, where the gas enters, is supposed to be substantially free of iron sulfide. According to Bueb, its contents are yellow to brown in color and have a cyanogen content of 13.5 percent (reckoned as Prussian blue), and an ammonia content of 6 to 7 percent. Such a light-colored product will oxidize in the air and turn blue, and therefore it is usually referred to in America as "blue mud." The mud is moved at regular intervals from one section to another, finished mud being discharged from the first section, and copperas solution being filled into the last one.

The finished mud is sold for its cyanogen and ammonia content, but in some

553 Nauss, O., *J. Gasbeleucht.*, **46**, 229–30 (1903).

554 Hand, A., *Z. angew. Chem.*, **18**, 1098–100 (1905).

555 Ost, H., and Kirschten, C., *ibid.*, **18**, 1323–4 (1905).

556 Guillet, O., *J. Gasbeleucht.*, **46**, 129 (1903), **47**, 208–9 (1904).

plants it is processed further in order to leave the ammonia with the coke plant or gasworks, and to save transportation costs where long haulage is necessary. According to Bueb, the slurry is simply boiled and then filtered, yielding an impure ammonium sulfate solution and a filter cake containing about 30 percent "blue," equivalent to 44 percent yellow prussiate.

plants break even and some make a little. The chief complaint has been that the ammonia contained in the mud was paid for by the chemical factories at a rate considerably lower than that for ammonia liquor, the product, almost exclusively made by the gasworks. Since about one-third of the total ammonia production of the gas plants operating the Bueb process went
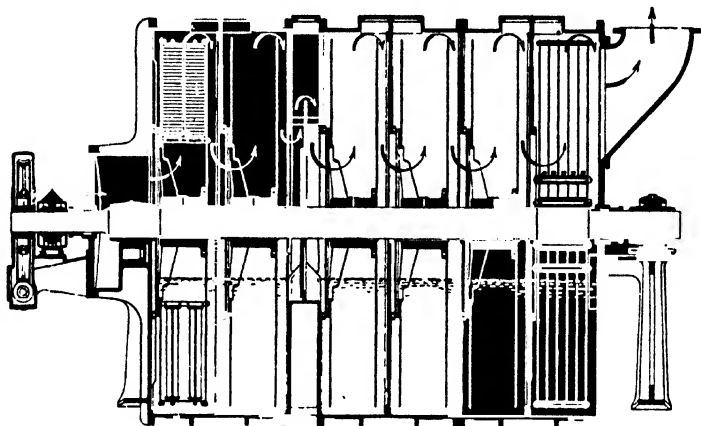
FIG. 12. Bueb scrubber.

Numerous reports on the Bueb process have appeared in the literature.[440, 443, 445, 446, 447, 450, 452, 467, 475, 476, 551, 556, 557] The paper by Mueller[152] is noteworthy because it gives a detailed account of an American Bueb installation. It is replete with theoretical considerations, literature references, pictures, and operating data. From a study of these reports it appears that a 96 percent cyanogen removal from the gas can be achieved without difficulty. As far as economics are concerned, most authors agree that little money is to be made from the process, aside from the intangible benefits derived from a cleaner gas; some

into the mud, such a price differential entailed heavy losses. Today, at the prevailing low ammonia prices, this consideration should be of no moment. Moreover, many modern coke plants are of sufficient size to make feasible a conversion of the blue mud to prussiates at the point of production.

To work up blue mud, it is generally boiled with lime, whereby all the ammonia is expelled and calcium ferrocyanide is formed. After filtration from the gypsum, the prussiate solution is treated with sodium sulfate, or, better, carbonate, solution; the calcium sulfate or carbonate is filtered off; and the sodium ferrocyanide solution is concentrated and crystallized. Potas-

557 Bueb, J., J. Gasbeleucht., 44, 115 (1901); Körting, ibid., 46, 1080 (1903), 47, 45-6 (1904).

sium salt is usually made by adding potassium chloride to the calcium solution, whereby the insoluble double salt calcium potassium ferrocyanide is precipitated. This is easily converted to the potassium compound by treatment with potassium carbonate.

It is perhaps of interest to note here that the practical success of the Bueb process led to a patent fight [558] in which Bueb's patent was attacked as invalid because of the older one of Knublauch, in which Knublauch specified ammonia as one of the useful alkalies. The suit was decided in favor of Bueb, largely because he had made ammonia a *conditio sine qua non,* whereas Knublauch merely mentioned it as permissible.

Antagonistic as Feld was toward the Bueb process, he nevertheless used its principle in his earliest process for the simultaneous removal of ammonia and hydrogen sulfide from gas.[559] It may be remembered from the ammonia section of this chapter that Feld scrubbed the gas with solutions of iron polythionates. From these solutions, iron sulfide is precipitated by the gas just as from the solution of any other iron salt, and the iron sulfide in turn reacts with the hydrogen cyanide of the gas to form soluble and insoluble ammonium-iron-cyanogen compounds. The soluble cyanide is precipitated by a careful addition of iron salt, and the insolubles are filtered off. They consist, just like the Bueb mud, of iron sulfide, iron cyanide, and ammonium ferroferrocyanide. On treatment with sulfur dioxide the iron sulfide is dissolved as polythionate (thiosulfate and tetrathionate), and the ammonia is removed from the cyanogen complexes as

ammonium sulfite, leaving Prussian blue behind.

Other patents belonging to this group are those of Bertelsmann and Becker [560] and of Coleman.[302] They are not important.

An excellent general paper by Gluud, Klempt, and Brodkorb [486] on the reasons for the frequently observed poor iron utilization in cyanide scrubbers and low yields of ferrocyanides is recommended for study.

These cyanogen-recovery processes are all based on the faculty of iron for forming numerous and stable complexes. Naturally the question arises whether closely related elements, such as cobalt, nickel, and manganese, have been proposed for the same purpose. They have been, but no such suggestion ever got beyond the experimental stage.

Even Knublauch, in his old patent,[516] mentioned that manganese and zinc could be used instead of iron, but this remained just a suggestion. Feld [548, 561] advocated in a number of patents the use of manganese, zinc, and lead. Though not practical, his suggestions are of theoretical interest and will be discussed below under the heading of hydrogen cyanide production from gas. Bergh [562] proposed cleaning coal gas with the aid of the liquid residues from copper extraction, which contain zinc, iron, and sodium chloride. A mixture of sulfide and cyanide is produced, which is separated by the addition of a weak alkali. Sperr [563] washed the gas with a solution of sodium zincate, thereby producing sodium zinc cyanide and zinc sulfide. The cyanide com-

558 Knublauch, O., and Bueb, J., *ibid.,* 46, 769-71 (1903).

559 Feld, W., Ger. Pat. 244,487 (1910).

560 Bertelsmann, W., and Becker, A. C., Ger. Pats. 415,206 (1923), 478,676 (1927).

561 Feld, W., Ger. Pats. 141,624 (1904), 176,-746 (1906).

562 Bergh, C. A., Ger. Pat. 272,094 (1912); *Gas World,* 60, 620 (1914).

563 Sperr, F. W., Jr., U. S. Pat. 1,213,429 (1927).

plex was destroyed by the addition of sodium sulfide, and sodium cyanide was recovered from the solution.

More knowledge is available concerning the use of nickel salts. Gluud and Riese [564] wrote an interesting paper on this subject and also patented the process. According to these authors nickel salts remove hydrogen cyanide from gases by first forming a sulfide and finally a double cyanide:

$$NiS + 2NH_4CN \rightarrow (NH_4)_2S + Ni(CN)_2$$

$$Ni(CN)_2 + 2NH_4CN \rightarrow (NH_4)_2Ni(CN)_4$$
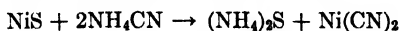
This reaction is analogous to the corresponding iron reaction, except that only two ammonium cyanide moles are built into the complex, against the four moles for iron. The presence of ammonia in the gas is apparently detrimental, giving rise to thiocyanate formation by rearrangement of the nickel complex, and therefore soda or potash is preferred as the alkali. Since their nickel-cyanogen complexes show much greater solubilities, they are technically more desirable anyway. The solid salts $Na_2Ni(CN)_4$ or $K_2Ni(CN)_4$ can be readily separated from the spent liquors by crystallization, but the recovery of the nickel salt from them is not as yet commercially feasible. An important advantage of the process is that the carbon dioxide of the gas does not destroy the complexes.

FORMATION OF COMPLEX COPPER SALTS

Of much greater importance, and endowed with better economic prospects, is the use of copper and copper salts. It was first proposed by von der Forst [565] and is based, as are all the other suggestions mentioned in this chapter, on the formation of complex salts. According to the inventor, the end product is much purer than the corresponding iron compounds. In carrying out the process, the copper salt solution is allowed to flow, drop by drop, into an alkaline-earth or alkali hydroxide or ammonia solution through which the gas being treated flows; thereby a precipitation of copper sulfide is prevented, and a complete absorption of the cyanogen is effected in a clear solution. As an alternative, metallic copper is placed around the openings from which the gas issues. When ammonia liquor is used in the process it should contain over 3 percent ammonia. The compounds formed, according to Gluud and Jacobson,[12] are $NH_4CN \cdot CuCN$ or $(NH_4)_3$-$Cu(CN)_4$.

A number of modifications have been suggested in subsequent patents.[566] The concentration of ammonia in the cyanogen scrubber was increased by adding ammonia from the stills, and the total outlay for copper salts was reduced by using copper ores, residues from copper smelting, and especially the copper cyanide which remained after working up the copper-cyanogen complex into hydrogen cyanide and ammonium sulfate with the aid of sulfuric acid. A patent to the Gesellschaft für Kohlentechnik [567] contemplated converting this residual copper cyanide to ammonium thiocyanate with the aid of copper sulfide and ammonium sulfide. This would seem to be an expensive way of making ammonium thiocyanate, since it can be made so easily and cheaply by much more direct processes, which will be reported below.

There were few other workers in this

564 Gluud, W., and Riese, W., Ger. Pat. 551,-074 (1929); *Ber. Ges. Kohlentech.*, 3, 437–51 (1931).

565 Von der Forst, P., Ger. Pat. 182,084 (1906).

566 C. Otto & Co., Ger. Pat. 201,001 (1907). Von der Forst, P., Ger. Pats. 280,652 (1913), 361,324 (1921).

567 Gesellschaft für Kohlentechnik m.b.H., Ger. Pat. 358,022 (1920).

field. Bergfeld [568] took out a rather confused patent in which he proposed to use anhydrous copper sulfate together with other salts, such as alkaline-earth sulfates or chlorides. In a paper describing his process he says that cyanogen of the gas is fixed as cuprous ammonium cyanide. However, the problem was extensively investigated by Mueller. It appears from his main patent [569] that, if cupric compounds are used, some of the hydrocyanic acid is lost as cyanogen:

$$CuCO_3 + H_2S \rightarrow CuS + H_2O + CO_2$$

$$2CuS + 2Na_2CO_3 + 8HCN \rightarrow$$
$$2Na_2Cu(CN)_3 + 2H_2S + 2CO_2$$
$$+ (CN)_2 + 2H_2O$$
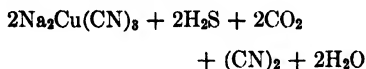
If, however, a cuprous salt is used, such loss can be avoided:

$$Cu_2S + 2Na_2CO_3 + 6HCN \rightarrow$$
$$2Na_2Cu(CN)_3 + H_2S + 2CO_2 + 2H_2O$$

The same result can be achieved by the use of a cupric salt and free copper:

$$CuS + Cu + 2Na_2CO_3 + 6HCN \rightarrow$$
$$2Na_2Cu(CN)_3 + H_2S + 2CO_2 + 2H_2O$$

The solution of disodium cuprous cyanide obtained in thus scrubbing the gas is evaporated under vacuum to expel hydrogen sulfide, the solid compound crystallizing from the concentrated solution. If copper carbonate is added to the solution before evaporation, the original complex is converted to a simpler one, again with the loss of cyanogen:

$$6Na_2Cu(CN)_3 + 2CuCO_3 \rightarrow$$
$$8NaCu(CN)_2 + 2Na_2CO_3 + (CN)_2$$

Loss of cyanogen is again avoided by having free copper present or by using a cuprous salt entirely:

$$4Na_2Cu(CN)_3 + CuCO_3 + Cu \rightarrow$$
$$6NaCu(CN)_2 + Na_2CO_3$$
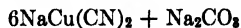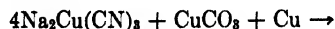
The monosodium cuprous cyanide obtained in this manner may be used again in the absorption step:

$$6NaCu(CN)_2 + H_2S + Na_2CO_3 \rightarrow$$
$$4Na_2Cu(CN)_3 + Cu_2S + CO_2 + H_2O$$
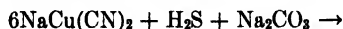
As alternative methods of working up the disodium complex, its solution may be treated with zinc salt, yielding sodium cuprous cyanide and zinc sodium cyanide; or with cupric sulfate and sulfur dioxide, yielding cuprous cyanide; or with sulfuric acid, yielding hydrocyanic acid and copper cyanide. If the absorption stage of the process is carried out with gas containing ammonia, the use of soda ash can be dispensed with. The ammonia is then eventually recovered as ammonium sulfate.

Other patents of Mueller [570] deal specifically with the application of the process to ammoniacal gas, the establishment of a cyclic scheme, and the production of pure hydrocyanic acid. The gas is treated with cuprous sulfide:

$$Cu_2S + 6HCN + 8NH_3 + CO_2 + H_2O \rightarrow$$
$$2(NH_4)_2Cu(CN)_3 + (NH_4)_2S + (NH_4)_2CO_3$$
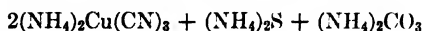
The resultant solution is boiled (with addition of cuprous cyanide from a later stage), whereby excess hydrogen sulfide and carbon dioxide are expelled, and cuprous sulfide is precipitated:

$$2(NH_4)_2Cu(CN)_3 + (NH_4)_2S + (NH_4)_2CO_3$$
$$+ 6CuCN \rightarrow$$
$$6NH_4Cu(CN)_2 + Cu_2S + 2NH_3 + CO_2 + H_2O$$

[568] Bergfeld, L., Ger. Pat. 255,593 (1910) ; J. Gas Lighting, 122, 385 (1913).
[569] Mueller, M. E., U. S. Pat. 1,413,762 (1922).
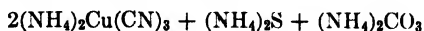
[570] Mueller, M. E., Brit. Pat. 190,961 (1922) ; U. S. Pat. 1,413,763 (1922).

The cuprous sulfide goes back into the absorption stage, and the solution of ammonium cuprous cyanide is distilled with sulfuric acid to yield hydrocyanic acid and cuprous cyanide, which is added to the boiling stage, and in some cases also to the scrubbing solution:

$$6NH_4Cu(CN)_2 + 2NH_3 + 4H_2SO_4 \rightarrow$$
$$6CuCN + 4(NH_4)_2SO_4 + 6HCN$$
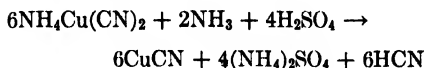
The important point in this cyclic process is the necessity of having present in solution at least two atoms of copper for each molecule of hydrogen sulfide, so that in the acidification step no hydrogen sulfide will be evolved with the hydrogen cyanide.

Another paper by Mueller [571] gives further details of the process as to its operation, yields, and production costs. It points out that cheap copper-bearing materials, such as copper scale and copper matte, can be used, and that copper losses are small—about 1 pound of cuprous cyanide for every 3,000 pounds recovered.

The mechanism of the process does not seem to have been cleared up completely by Mueller's work, for there are a number of discrepancies, and the formulas of the copper-cyanogen complexes also need verification. In general, the chemistry of the copper process bears a strong resemblance to that of the iron-cyanogen complexes, and analogies with certain steps in the Bueb process and its modifications are unmistakable.

Gluud and Riese [564] assigned the formula $(NH_4)_3Cu(CN)_4$ to the main compound of this process, and they stated that the whole scheme is greatly handicapped by its sensitivity to carbon dioxide. They also pointed out that the scrubbing efficiency decreases materially with increasing concentration of the double cyanide; but this should have no bearing on the cyclic Mueller process in which the double cyanide is destroyed in each cycle so that it cannot build up.

CYANOGEN REMOVAL AS THIOCYANATES

The wet cyanogen-recovery methods described above were more or less based on knowledge gained in the operation of dry iron oxide boxes. They are all rather complicated and usually yield a mixture of products. Another but simpler method, also based on dry-box operation, utilizes the strong affinity of cyanogen for sulfur. It has already been pointed out that, when sufficient ammonia is left in the gas, all hydrocyanic acid will be removed in the dry boxes as thiocyanate. Under such conditions, the sulfur stored in the boxes from the regeneration step will react with the ammonia, hydrogen sulfide, and hydrogen cyanide of the gas with the formation of ammonium thiocyanate. The thought of separating the thiocyanate production from the dry-box operation is a natural one; it is, indeed, just about as old as the iron-cyanogen-removal processes.

According to patents by the British Cyanides Company [572] and by Smith, Gidden, Salamon, and Albright,[572] gas is cooled, after tar removal, and passed into a scrubber containing a slurry of sulfur in ammonia liquor. A solution of ammonium polysulfide is quickly formed:

$$2NH_3 + H_2S + xS \rightarrow (NH_4)_2S_{x+1}$$

which reacts with the hydrocyanic acid of the gas:

$$(NH_4)_2S_{x+1} + HCN + NH_3 \rightarrow$$
$$NH_4SCN + (NH_4)_2S_x$$
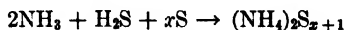
[571] Mueller, M. E., *Chem. & Met. Eng.*, **30**, 978–80 (1924).
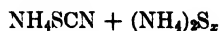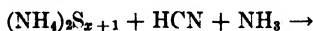
[572] British Cyanides Co. Ltd., Ger. Pat. 136,-397 (1901). Smith, W., Gidden, W., Salamon, A. G., and Albright, G. S., Brit. Pat. 18,653 (1902).

By constant addition of sulfur the process is caused to go continuously, only the cyanogen and an equivalent quantity of ammonia being removed from the gas, while the hydrogen sulfide goes on unchanged once equilibrium has been established. After a sufficient concentration has been reached, the liquor is evaporated to recover solid ammonium thiocyanate. Some very similar patents were taken out by Chance,[573] who separated the scrubbing stage into two steps, using first ammonium polysulfide, followed by a sulfur slurry.

The original process has survived practically unchanged to the present day. What modifications exist are of minor importance and do not touch the basic principle. Carpenter [574] simply substituted lime for the ammonia and used a large excess of it, but he worked on gas which still contained ammonia. Tscherniac [575] also used lime, but he operated with ammonia-free gas. In another patent,[576] Tscherniac added sodium sulfate to his lime-sulfur mixture, apparently making some sodium thiocyanate. The Fabriques de produits chimique de Thann et Mulhouse [577] proposed using an aqueous mixture of calcium salts on ammonia-free gas. Carpenter and Somerville and also Tscherniac [578] proposed furthermore to prepare magnesium thiocyanate by using magnesia or magnesium carbonate instead of lime. Williams [579] suggested utilizing the sulfur contained in spent oxide.

The original process and its practical operation have been described in detail by Anon.[580] According to this publication, 90 percent of the cyanogen contained in the gas is removed as ammonium thiocyanate. The process is simple, but it is necessary to have in the crude gas an excess of ammonia over that required by theory, and in case of need ammonia liquor must be fed to the cyanogen scrubber. A high percentage of carbon dioxide in the gas is detrimental to the process, unless the hydrogen sulfide content also is fairly high, because it tends to drive the hydrogen sulfide out of the solution and thus decreases the amount of ammonium polysulfides made. Broadberry [581] also described the process, and the subject has been taken up again more recently by Gluud and his collaborators.[442, 582] These investigators worked out the process in very great detail, particularly for coke-oven practice, and they studied the scrubbing efficiency as influenced by gas temperatures, gas velocities, liquor concentration, concentration of ammonia and hydrogen sulfide in the liquor, sulfur excess, and other factors. Their profuse operating data have been summarized by Gluud and Jacobson [12] as shown in Table XXVIII.

It is apparent from the table that when total cyanogen removal is desired the liquor should be withdrawn when it reaches a concentration of about 20 percent, as was done in early English practice. On the other hand, a concentration of 30 percent can be reached without much difficulty and with tolerable efficiency, if desired. Hansen [583] advocated further concentration of the liquor by using it to scrub the gas,

573 The British Cyanides Co. and Chance, K. M., Brit. Pat. 6,218 (1908); U. S. Pat. 922,564 (1909).
574 Carpenter, C. C., Brit. Pat. 22,710 (1903).
575 Tscherniac, J., Brit. Pat. 2,708 (1906); Ger. Pat. 192,534 (1906).
576 Tscherniac, J., U. S. Pat. 862,678 (1907).
577 Fabriques de produits chimique de Thann et Mulhouse, Fr. Pat. 373,986 (1907).
578 Carpenter, C. C., and Somerville, J. M., Brit. Pat. 8,166 (1903). Tscherniac, J., Brit. Pat. 24,767 (1903).
579 Williams, P. E., Brit. Pat. 23,624 (1909).

580 Anon., J. Gas Lighting, 84, 218-20 (1903).
581 Broadberry, A. E., ibid., 120, 31-4 (1912).
582 Gluud, W., and Klempt, W., Z. angew. Chem., 40, 659-60 (1927).
583 The Koppers Co. of Delaware, Fr. Pat. 729,140 (1931).

TABLE XXVIII

HYDROCYANIC ACID ABSORPTION TEST ON A LARGE PLANT EMPLOYING THE SULFOCYANIDE PROCESS [12]

Days	Gas Volume thousand cubic feet per hour	NH₄SCN Content of the Solution percent	Hydrocyanic Acid Before the Washer	After the Washer	Absorption percent
			grains per 100 cubic feet		
1	83.3	2.0	22	.....	100
2	160.0	3.8	24	0.488	98
3	110.0	5.7	20	0.309	98.5
5	91.3	9.8	19	0.244	98.7
8	87.4	15.6	25	0.122	99.5
10	87.4	19.0	30	0.284	99.0
12	98.8	21.9	25	0.244	99.1
14	98.8	25.7	32	3.050	90.4
17	91.3	30.1	33	6.620	79.6

from which tar, hydrogen cyanide, etc., already had been removed. In another patent,[584] the same inventor dealt with naphthalene removal from the gas before it enters the cyanogen scrubber. In two further patents [585] he suggested that the polysulfide solution used should be of an order higher than the disulfide, and should be at a temperature above 30° C. Klempt, Brodkorb, and Erlbach [586] attempted to utilize ammonium thiosulfate instead of free sulfur, but found it not feasible, since high partial pressures of hydrogen sulfide and carbon dioxide prevented the formation of ammonium cyanide and thus of ammonium thiocyanate.

The Minot process,[459] though frequently hailed as unique, offers nothing really new, inasmuch as in its essentials it merely contemplates binding hydrogen cyanide as thiocyanate with the aid of sodium polysulfide instead of with the customary ammonium compound. As an addition, the process removes carbon disulfide as ammonium trithiocarbonate, which later on is said to be converted to ammonium thiocyanate and finally to sodium thiocyanate.

Instead of adding sulfur from an extraneous source, Brodkorb, Keller, and Klempt [587] proposed forming it in situ from the hydrogen sulfide of the gas, basing their proposal on the discovery of Gluud and Riese,[564] referred to above, that nickel-cyanogen complexes in the presence of ammonia are easily converted to thiocyanate. They found that, if small amounts of nickel compounds are added to the liquors with which the gas is scrubbed, an amount of hydrogen sulfide corresponding to the hydrogen cyanide will be oxidized to sulfur, provided that there is enough oxygen in the gas. The gas thus furnishes the sulfur necessary for the conversion of the hydrogen cyanide to ammonium thiocyanate. In order to avoid production of ammonium thiosulfate it is necessary to adjust the quantity of nickel added to the quantity

584 Hansen, C. J., U. S. Pat. 1,908,633 (1933).
585 Hansen, C. J., Fr. Pat. 731,970 (1931); U. S. Pat. 1,924,206 (1933).
586 Klempt, W., Brodkorb, F., and Erlbach, H., Ber. Ges. Kohlentech., 3, 493–6 (1931).

587 Brodkorb, F., and Keller, K., Ger. Pat. 559,171 (1930). Klempt, W., and Brodkorb, F., Ger. Pat. 565,408 (1931). Klempt, W., Ger. Pat. 590,310 (1934); U. S. Pat. 2,008,253 (1935).

of oxygen contained in the gas. Loss of nickel as nickel-cyanogen complex, which is not active as a catalyst, is avoided by periodically adding ammonium sulfide or by lowering the solution temperature.

Of theoretical interest are two minor applications of the principle of removing cyanogen as thiocyanate. Keller [588] found that, when treating crude light oil to remove therefrom hydrogen sulfide and hydrogen cyanide, the hydrogen cyanide was eliminated in the form of ammonium thiocyanate by adding a small amount of ammonia and subsequently oxidizing. The Badische Anilin und Soda Fabrik [589] found that, in removing hydrogen sulfide and ammonia from gas by means of active carbon (plus oxygen), residual hydrocyanic acid of the gas was fixed in the carbon as ammonium thiocyanate.

This finding leads us to a broad consideration of gas-purification methods which are primarily devoted to the removal of hydrogen sulfide, but which at the same time eliminate substantial quantities of cyanogen. It is evident from the foregoing discussion that, whenever a strong alkali, sulfur, hydrogen sulfide, and hydrocyanic acid meet, the formation of thiocyanate is inevitable; and these conditions prevail in a majority of the processes removing hydrogen sulfide. On account of the acid nature of hydrogen sulfide the gas is best treated with alkaline liquors, and, since for regeneration the foul liquors are usually blown with air, the necessary sulfur is furnished at all times. A detailed discussion of the various sulfur-removal processes is contained in Chapter 26 and also in another section of this chapter, so that only the barest outlines will be given here.

[588] Keller, K., *Ber. Ges. Kohlentech.*, **3**, 429–30 (1931).
[589] Badische Anilin und Soda Fabrik, Brit. Pat. 190,203 (1921).

The simplest processes use weakly alkaline solutions for scrubbing the gas, such as solutions of ammonia or sodium carbonate, and the so-called Seaboard process may well be taken as typical. This process employs a sodium carbonate solution of about 3 percent strength which absorbs from the gas all acidic components, i.e., carbon dioxide, hydrogen sulfide, and hydrogen cyanide.

(1) $Na_2CO_3 + CO_2 + H_2O \rightleftarrows 2NaHCO_3$

(2) $Na_2CO_3 + H_2S \rightleftarrows NaHS + NaHCO_3$

(3) $Na_2CO_3 + HCN \rightleftarrows NaCN + NaHCO_3$
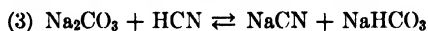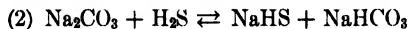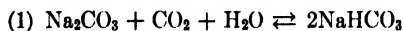
On aeration of the foul solutions these reactions are supposed to be reversed, whereby carbon dioxide, hydrogen sulfide, and hydrogen cyanide are liberated and blown out by the air. However, in practice a substantial amount of oxidation of the hydrogen sulfide takes place, and as end products there appear in the solutions sodium thiosulfate and sodium thiocyanate. Sperr [590] wrote a lengthy paper on this subject, with profuse details. It is referred to for study. Other papers dealing solely or partially with this process are those of Sperr,[462] Beebe,[591] Cook,[591] Ramsburg,[591] Davey,[591] and Jacobson and Carvlin.[592] The patents are numerous.[593] It appears that this process reduces the cyanogen con-

[590] Sperr, F. W., Jr., *Proc. Am. Gas Assoc.*, **1921**, 282–363.
[591] Beebe, A. M., et al., *Gas Age-Record*, **49**, 741–3 (1922). Cook, T. R., *Gas J.*, **172**, 432–7 (1925). Ramsburg, C. J., *Gas Age-Record*, **63**, 205–6, 213–6 (1929). Davey, W. J. G., *Gas J.*, **189**, 157–9 (1930).
[592] Jacobson, D. L., and Carvlin, G. M., *Proc. Am. Gas Assoc.*, **1932**, 1022–9.
[593] Ramsburg, C. J., U. S. Pats. 1,389,980 (1921), 1,486,196 (1922). Koppers Co., Brit. Pats. 190,116–7, 190,119 (1922), 190,131, 207,-488, 210,382 (1927); Ger. Pat. 492,522 (1927). Fulweiler, W. H., U. S. Pat. 1,589,749 (1926). Sperr, F. W., Jr., U. S. Pat. 1,592,648 (1926). I. G. Farbenindustrie A.-G., Brit. Pat. 321,982 (1928).

tent of the gas to less than 1 grain per 100 cubic feet, but probably only a comparatively small amount is actually recovered as thiocyanate, the larger share being expelled by the actifier air.

The very similar process of Petit [594] uses a potassium carbonate solution but is the same as far as cyanogen removal is concerned.

Taplay's process,[457, 506] which was referred to above, uses calcium or magnesium carbonate (or bicarbonate), but employs no air blowing and yet claims the production of ammonium thiocyanate. This can be accounted for only on the assumption that there is enough oxygen in the gas to furnish free sulfur in a nascent state. Perhaps impurities of iron and similar active agents contained in the chalk employed in the process serve as catalysts in this oxidation.

The polythionate processes of Feld [412] and Overdick,[357] though designed primarily for the simultaneous recovery of hydrogen sulfide and ammonia, also remove hydrogen cyanide in the step of washing the gas with tri- and tetrathionates. Although in discussions of the Feld process this is rarely mentioned, it was considered a decided disadvantage, inasmuch as the resulting ammonium thiocyanate discolored the recovered ammonium sulfate red. This was pointed out by Funcke.[314] In the Overdick modification of the Feld process, this fact was well recognized, and a special effort was made to remove all the cyanogen from the gas by having enough ammonia present. The final liquors, after heating and separation of sulfur, consisted of ammonium sulfate and ammonium thiocyanate, which were separated by fractional crystallization.[357]

Closely related to the Seaboard process described above are those processes in which metallic oxides or salts (largely iron) are used together with alkaline solutions as scrubbing liquors. The metal additions may be very sizable or merely constitute catalytic amounts. In any event, the gas is scrubbed with these liquors to absorb hydrogen sulfide, and alkali sulfides and metal sulfides are formed as a result. When such fouled solutions are blown with air the hydrogen sulfide is not expelled as such, as in the Seaboard process, but is oxidized to free sulfur, thiosulfate, etc. Under these conditions any hydrogen cyanide present in the solution or absorbed in the next scrubbing cycle is, of course, converted to the thiocyanate of the alkali used.

Harcourt [595] was perhaps one of the very first to practice such a process. He scrubbed the gas before ammonia removal with iron oxide suspended in water, and activated the foul slurry by air blowing. Though he did not say so specifically, he doubtless made ammonium thiocyanate in this way.

Burkheiser [318, 319, 320] in the later modifications of his process scrubbed the gas with an ammoniacal suspension of iron hydroxide, oxidized the iron sulfide with air to regenerate the active iron material and produce free sulfur, and in so doing removed the cyanogen from the gas in the form of ammonium thiocyanate.

Later developments along the line of Burkheiser (but devoted solely to the removal of hydrogen sulfide) are the Koppers Ferrox process, using sodium carbonate and iron hydroxide, and the iron process of the Gesellschaft für Kohlentechnik using the ammonia of the gas and iron hydroxide. Analogous processes using nickel or copper were developed by both companies, but gas free of cyanogen was pre-

[594] Petit, T., *J. Gas Lighting*, **131**, 645–6 (1915) ; *Gas World*, **63**, 374 (1915).

[595] Harcourt, A. G. V., *J. Gasbeleucht.*, **18**, 678 (1875).

ferred for them, since the regeneration of the nickel-cyanogen complexes is not so simple, although Klempt [587] showed that it can be done. The Ferrox process recovers 100 percent of the cyanogen in the gas as sodium thiocyanate,[12] and the other processes should do likewise. Patents in this field are numerous,[596] and for details Chapter 26 should be consulted.

Very similar to these processes, though not employing iron oxides, is the one of Smith and Pryde.[597] These inventors scrubbed the gas with a suspension of ferric ferrocyanide, which was reduced by the hydrogen sulfide to ferrous ferrocyanide and ammonium ferrocyanide, the hydrogen sulfide itself being oxidized to free sulfur. By blowing with air, the original ferric ferrocyanide was reformed. Owing to the formation of sulfur, the hydrogen cyanide of the gas was converted to ammonium thiocyanate. Pieters [528] considered this scheme a modified Ferrox process and said that the hydrogen cyanide recovery is about 90 percent.

A radical departure from the foregoing procedure, as far as hydrogen sulfide removal is concerned, was brought about by the development of the Thylox process. It is based on the discovery that thioarsenate solutions will oxidize hydrogen sulfide to sulfur, which remains in the molecule until liberated by aeration:

$$Na_3AsO_2S_2 + H_2S \rightarrow Na_3AsOS_3 + H_2O$$

$$Na_3AsOS_3 + O \rightarrow Na_3AsO_2S_2 + S$$

Since the solution is weakly alkaline (soda ash or ammonia) the hydrogen cyanide is also removed from the gas, as sodium thiocyanate, with an efficiency of 100 percent. The process has been well described in the technical press and patent literature.[598]

The simultaneous removal of hydrogen sulfide, hydrogen cyanide, and ammonia from gas has the great disadvantages of often creating operating difficulties, such as using up catalytic amounts of copper, nickel, etc., and of producing mixtures of compounds which are difficult to work. For either or both of these reasons a number of investigators separate the cyanogen removal from the rest of the process, normally using it as the first stage. Invariably ammonium or sodium thiocyanate is produced in this way. Split processes of this type are described in a number of papers and patents.[353, 366, 599]

In concluding this section a few patents and papers may be mentioned which have to do with the production of pure thiocyanates from the various crude solutions obtained in these processes. Even in the simplest process, where ammonium thiocyanate is produced for its own sake by scrubbing gas with an ammoniacal sulfur slurry, it is not recovered directly in pure form on evaporation and crystallization of the liquor. It contains considerable quan-

J., **207**, 307–9 (1934) ; *J. Soc. Chem. Ind.*, **53**, 657–60 (1934).

[598] Jacobson, D. L., and Gollmar, H. A., Brit. Pat. 280,165 (1926). Gollmar, H. A., Brit. Pat. 286,633 (1927) ; U. S. Pats. 1,719,762, 1,719,177 (1929) ; *Ind. Eng. Chem.*, **26**, 130 2 (1934). Jacobson, D. L., *Gas Age-Record*, **63**, 597–600 (1929) ; U. S. Pats. 1,719,180 (1929), 1,852,014 (1932). The Koppers Co., Fr. Pat. 727,206 (1931). Fitz, W., *Brennstoff-Chem.*, **19**, 397–402 (1934).

[599] Sperr, F. W., Jr., U. S. Pat. 1,806,370 (1931). Davies, C. J., U. S. Pat. 1,942,050 (1933). Gollmar, H. A., U. S. Pat. 1,971,779 (1934). Bähr, H., Mengdehl, H., and Wenzel, W., Ger. Pat. 639,193 (1938). I. G. Farbenindustrie A.-G., Brit. Pat. 479,301 (1938).

[596] Koppers Co., Brit. Pats. 238,172, 241,221 (1924). Reeson, J. N., and Moss, W. L., Brit. Pat. 249,312 (1925). Koppers Co., Brit. Pats. 255,140, 255,144 (1925). Sperr, F. W., Jr., and Jacobson, D. L., U. S. Pat. 1,656,881 (1928). Jacobson, D. L., U. S. Pats. 1,741,113, 1,792,097 (1931). D'Leny, W., Park, J. R., and Imperial Chemical Industries, Ltd., Brit. Pat. 330,381 (1929).

[597] Smith, F. F., and Pryde, D. R., *Gas World*, **100**, No. 2592, Coking Sect., 14–6 (1934) ; *Gas*

tities of thiosulfate, which Keller[600] destroyed with sulfuric acid, and of soluble ferrocyanides, which Gluud, Keller, and Klempt[601] converted to insoluble complexes by heating above 100° C. A very fine, comprehensive paper on ammonium thiocyanate—its history, methods of manufacture, physicochemical properties, reactions, and uses—has been contributed by Shnidman.[602] Waste solutions obtained from sulfur-removal processes such as the Seaboard, Ferrox, and Thylox processes contain largely sodium thiosulfate and thiocyanate. Darrin[603] separated these salts by evaporating the liquor to a boiling point of 130 to 135° C, cooling to crystallize out the thiosulfate, evaporating further, and recovering the thiocyanate either in the anhydrous form or as the dihydrate, depending on the conditions. Hall[604] evaporated such waste liquor to dryness and extracted the thiocyanate with alcohol, in which thiosulfate, sulfate, carbonate, and other impurities are not soluble. Fulton[605] treated the liquor with a soluble alkaline-earth salt, such as calcium chloride, and heated to such a point, about 110° C, that the alkaline-earth thiosulfate was decomposed to the insoluble alkaline-earth sulfite and to sulfur. Calcium thiocyanate was recovered after filtering off the insolubles.

There are many papers of general interest in connection with the recovery of cyanogen either as complex iron cyanides or as thiocyanates.[82, 161, 456, 473, 479, 606] All the cyanogen-recovery processes enumerated above are afflicted with the same weakness: they produce compounds which have only a limited market. This is true of the prussiates as well as of the thiocyanates, and the valiant attempts to open up new outlets for them have not been crowned with success. The best that could be done in the past was to convert them to cyanides, for which the market is a great deal better. However, the processing costs were so high that these cyanides could not compete with those made from beet-sugar molasses, from sodium amide, and from calcium cyanamide. It is only too natural, therefore, that inventors endeavored to produce cyanides or hydrocyanic acid more directly from coal-carbonization gases.

The first idea was to split the ferrocyanides with acid, but this releases only one-half of the hydrogen cyanide which they contain, and clever cyclic schemes like those of Espenhahn[533] and Sperr,[534] which have been described above in detail, could not change the situation materially. Mueller[607] and Williams[417] thought that they could increase the amount of hydrocyanic acid liberated on acidification by having copper or copper salts present, but they doubtless did not succeed in getting enough more to make the process worth while. Feld,[608] at a very early date, had recognized the problem and devised a system by which he actually could release all the hydrogen cyanide. It was based on his analytical procedure, which is recognized as the best in existence, and contemplated converting the prussiates to mercury cyanide, which in turn can be split quantitatively by distillation with acid. He gave

600 Keller, K., U. S Pat. 1,908.515 (1933).
601 Gluud, W., Keller, K., and Klempt, W., Ger. Pat. 511,575 (1927).
602 Shnidman, L., *Am. Gas Assoc., Chem. Com. Rep.*, 1932, pp. 5–23.
603 Darrin, M., U. S. Pats. 1,570,047, 1,584,852 (1926).
604 Hall, R. E., U. S. Pat. 1,648,224 (1927).
605 Fulton, R. R., Can. Pat. 284,068 (1928) ; U. S. Pat. 1.751,274 (1930).
606 Espenhahn, E. V., *Chem. and Met. Eng.*, 30, 629–31 (1924). Proteus, *Gas World*, 10, 447–52 (1934).
607 Mueller, M. E., U. S. Pat. 1,347,518 (1920).
608 Feld, W., Ger. Pat. 141,024 (1901) ; Brit. Pat. 24,920 (1901).

the following fundamental equation for the process:

$$2K_4Fe(CN)_6 + 8HgCl_2 \rightarrow$$

$$6Hg(CN)_2 + Fe_2Cl_6 + Hg_2Cl_2 + 8KCl$$
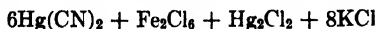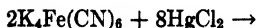
Though the process doubtless worked, it was too cumbersome and was moreover burdened by the grave problem of recovering the costly mercury from the residues. It was never a commercial success. A very similar process was advocated by de las Fuentes.[609]

Feld[561] took a real step forward when he suggested washing the gas with solutions or suspensions of basic or neutral hydroxides, carbonates, or chlorides of such elements as magnesium or aluminum, which will absorb hydrogen cyanide when cold and give it off again when heated. Provisions were made to eliminate hydrogen sulfide and carbon dioxide from the gas prior to the hydrogen cyanide removal. This proposal is perhaps the first approach to the modern ideas on cyanogen recovery related below. They all have in common the removal of hydrogen cyanide from gas not in the form of cyanogen compounds but as such.

Percy and Byrom[610] proposed passing the gas through a scrubber against a very small trickle of water. Since hydrocyanic acid is miscible with water in all proportions, a complete recovery should thus be possible. This early observation remained unnoticed until Schwarz[465] made a fine study of it, determining the percentage recovery for various solution rates and temperatures, vapor pressures of the solutions obtained, saturation curves, and other interesting data. Haun[611] also scrubbed

with water, and distilled the dilute solution *in vacuo* under such conditions as to separate the small quantity of hydrogen sulfide dissolved by the scrubbing water from the aqueous condensate containing the hydrocyanic acid. An engineering study of steam-stripping hydrogen cyanide from dilute aqueous solutions was made by Krebs.[612] He pointed out that special metal must be used for the stripping tower to prevent decomposition of the hydrogen cyanide. The column which he used was described. Sperr[613] dispensed with the special water wash, using the water from the final coolers instead. Since this water contains some hydrogen sulfide besides the hydrogen cyanide, he separated the two to a large extent by aeration, which removes 90 percent of the sulfide and none of the cyanide. The remaining hydrogen sulfide was precipitated as zinc sulfide or destroyed by chlorine and other oxidizing agents which do not attack the hydrogen cyanide. Hydrogen cyanide was then precipitated as zinc cyanide, which was decomposed with acid to yield pure hydrocyanic acid.

In an alternative method, the final cooler water was aerated to remove most of the hydrogen sulfide and was then precipitated with nickel salt as nickel cyanide, which was obtained in concentrated form by the use of a Dorr thickener. Acidification and distillation again yielded hydrogen cyanide. To remove residual hydrogen sulfide, the sludge from the thickener might be treated with oxidizing agents such as permanganate or dichromate, which destroy the nickel sulfide contained in the nickel cyanide sludge. An even more practical proposal

609 De las Fuentes, J., Can. Pat. 153,466 (1914).

610 Percy, T. M., and Byrom, T. H., Brit. Pat. 1,608 (1908).

611 Haun, J. C., U. S. Pat. 1,742,505 (1930).

612 Krebs, O., *Chem. App.*, **19**, 50–3 (1932)

613 Sperr, F. W., Jr., Fr. Pat. 804,045 (1936); U. S. Pats. 2,088,003 (1937), 2,140,605 (1938); Brit. Pat. 461,130 (1937); Ger. Pat. 641,819 (1937).

by Sperr [614] contemplated washing the gas with water at less than 15° C—preferably at about 10° C—aerating the solution to remove most of the hydrogen sulfide, and driving off the hydrogen cyanide at 55 to 70° C with a current of inert gas which was passed over absorbents such as caustic soda. Hydrogen sulfide not removed in the aeration step might be removed by chemical treatment, as with copper sulfate, lead carbonate, etc.; or oxidizing agents such as chlorine and sulfur dioxide might be added to the air used for aeration.

<div align="center">RECOVERY OF CYANOGEN BY HOT
ACTIFICATION METHODS</div>

Although these processes recover only cyanogen from the gas, another group removes hydrogen sulfide at the same time, and is in fact devoted primarily to that purpose. In a general way these proposals are based on the removal of acidic substances from gas by means of alkaline solutions—salts of strong bases and weak acids or solutions of weak bases—with subsequent expulsion of the acidic substances by heating, "hot actification," or by passing an acid gas through them. Their chemistry is essentially the same as that of the Seaboard process, which has been outlined above, and is considered more in detail in Chapter 26.

One of the earliest suggestions in this group is that of Espenhahn,[615] who passed the gas through sodium carbonate-bicarbonate solutions, then heated this solution to expel a mixture of carbon dioxide, hydrogen sulfide, and hydrogen cyanide. The same result is probably obtained by Sperr and Hall,[616] who also used sodium carbon-

ate solution but activated it by heating under vacuum. Bragg [617] employed potassium borate, and Shaw [618] proposed sodium phenolate. Shaw's process has become quite prominent and is now widely used in industry, though chiefly for the removal of hydrogen sulfide. It has been described by Denig and Powell.[619] Zublin [620] used solutions of potassium phosphate of two different concentrations for the purpose, and Cole and Tannehill [621] utilized the ammonia of the gas as the alkaline agent. They worked in two stages, each time scrubbing with cool, dilute ammonia liquor, flash-distilling under vacuum without external application of heat, and finally obtained a mixture of ammonia, hydrogen sulfide, hydrogen cyanide, and a little carbon dioxide.

A very large number of compounds useful for this purpose has been suggested by Bähr and the I. G. Farbenindustrie. They may be divided into two groups: salts of strong inorganic bases and weak organic acids, and organic bases proper. The process using compounds of the first group has become very prominent in Europe under the name of Alkacid process. For practical purposes, alkali metal salts of amino acids are used, as of glycocoll, alanine, etc., but organic sulfonic acids have also been proposed.[622] These compounds may also be used in organic solvents rather than in aqueous solution, e.g., dissolved or suspended in a coal-tar cut boiling between 200 and 300° C.[623] This last patent added to the list of useful compounds qua-

[614] Sperr, F. W., Jr., Brit. Pat. 453,971 (1936); Ger. Pat. 636,330 (1936); U. S. Pat. 2,143,821 (1939).

[615] Espenhahn, E. V., U. S. Pat. 1,440,977 (1923).

[616] Sperr, F. W., Jr., and Hall, R. E., U. S. Pat. 1,533,773 (1925).

[617] Bragg, G. A., U. S. Pat. 1,920,626 (1933).

[618] Shaw, J. A., U. S. Pats. 2,028,124–5 (1936).

[619] Denig, F., and Powell, A. R., *Proc. Am. Gas Assoc.*, **1933**, 913–25.

[620] Zublin, E. W., U. S. Pat. 2,157,879 (1939).

[621] Cole, A. N., and Tannehill, A. L., U. S. Pat. 2,162,838 (1939).

[622] I. G. Farbenindustrie A.-G., Brit. Pat. 391,-780 (1933).

[623] I. G. Farbenindustrie A.-G., Fr. Pat. 765,-519 (1934).

ternary bases and salts of nitrophenols. The second group of the I. G. developments embraces pure organic bases such as alkylamines, alkylolamines, polyamines, and imines.[624] They are preferably used dispersed or dissolved in organic solvents, e.g., high-boiling petroleum or tar oils. As the last two patents enumerate a very large number of compounds, they should be studied for further details. In a good paper on the Alkacid process, Bähr[625] pointed out that by the proper choice of a scrubbing agent it is possible to differentiate between carbon dioxide, hydrogen sulfide, and hydrogen cyanide, so that the one or the other may be removed differentially from gases. A good example of such differentiation is presented by the Girdler process, which also uses organic bases for gas scrubbing, and which has attracted much attention in America. According to statements of the inventor himself and of others,[592, 626] the bases preferred by him, chiefly di- and triethanolamine, absorb carbon dioxide and hydrogen sulfide readily, but hydrogen cyanide not at all. Doubtless, it is necessary in all cases to balance carefully good absorption capacity (requiring strongly alkaline materials) against ease of actification (requiring weakly alkaline materials), and to select a base which is appropriate for the acid it is desired to recover. In general, the basic material employed should have an electrolytic dissociation less than that of the acidic gases which it is supposed to remove.

With the exception of the Bähr process, which employs differentiating absorbing compounds, most hot actification processes

recover a mixed gas, from which hydrogen cyanide must be separated if it is to be used as such or in the form of cyanides. The schemes of Haun[611] and Sperr[613, 614] are without question applicable to such a gas, and this subject is specifically treated by Schreiber.[627] He scrubbed with water the gas obtained on hot actification of a foul sodium phenolate liquor (after compression, if desired), whereby he absorbed all the hydrogen cyanide and very little of the hydrogen sulfide and carbon dioxide. The last two gases were removed by blowing with a current of clean coke-oven gas, and the purified hydrogen cyanide solution was distilled under vacuum, after acidification. The vaporized hydrogen cyanide was absorbed in caustic soda.

The preceding outline of hot actification processes has been intended as a survey rather than a complete enumeration, which must be left to the chapter on gas purification. A number of additional patents are listed here,[628] though the available abstracts do not specifically mention hydrogen cyanide. The nature of the compounds mentioned in these patents makes it probable that they should be useful for the purpose.

Instead of hot actification Petit[629] used regeneration by means of carbon dioxide. In his process weakly acidic gases, such as hydrogen sulfide and hydrocyanic acid, were absorbed by potassium carbonate solution. The foul solution was activated by passing into it carbon dioxide, which ex-

[624] I. G. Farbenindustrie A.-G., Brit. Pat. 417,-379 (1934). Bähr, H., Wenzel, W., and Mengdehl, H., U. S. Pat. 2,161,663 (1939).

[625] Bähr, H., *Refiner Natural Gasoline Mfr.*, 17, 237–44 (1938).

[626] Bottoms, R. R., *Ind. Eng. Chem.*, 23, 501–4 (1931); *Proc. Am. Gas Assoc.*, 1931, 1071–82.

[627] Schreiber, F. D., U. S. Pat. 2,219,713 (1940).

[628] Ulrich, H., Dehnert, H., and Fries, F. A., U. S. Pat. 2,011,386 (1935). I. G. Farbenindustrie A.-G., Brit. Pats. 457,343 (1936), 467,579 (1937), Fr. Pat. 811,473 (1937). Robinson Brothers Ltd., Parkes, D. W., and Evans, R. B., Brit. Pat. 468,972 (1937). Bähr, H., and Wenzel, W., U. S. Pat. 2,106,446 (1938). Gollmar, H. A., U. S. Pat. 2,163,169 (1939).

[629] Petit, T. P. L., Ger. Pats. 396,353 (1923), 471,042 (1928); Brit. Pat. 314,860 (1928).

pelled the two weaker acids and converted the carbonate to bicarbonate. Heating the bicarbonate solution regenerated carbonate and liberated carbon dioxide, which was used again in the next cycle. Petit used this process only for the removal of hydrogen sulfide, but it probably would be successful for the recovery of hydrogen cyanide, especially if the expelled gases were treated with water, as Schreiber [627] did with the hot actification gases. The Petit process is discussed in detail by several investigators.[630]

Water, as the simplest and cheapest solvent, has been utilized for the recovery of cyanogen, as related above; very little work has been done on the use of organic solvents for this purpose. Inasmuch as hydrogen cyanide is miscible with water in all proportions while it is much less soluble in almost any organic solvent, the use of organic solvents would not offer any practical advantages, especially in view of their much higher cost.

Felt [631] suggested washing coal gas, water gas, etc., with glycerol under pressure. He had in mind the removal of carbon dioxide and sulfur compounds, but doubtless removed hydrocyanic acid at the same time. The Société anon. pour l'industrie chimique à Bâle [632] extracted hydrogen cyanide from gaseous mixtures by scrubbing them with organic carboxylic acid esters, e.g., diethyl oxalate, phthalic esters, esters of cyanoacetic acid, and ethyl benzoate. The patent gives a tabulation showing the absorption power of various esters. Millar and Groll [633] employed esters and ethers of

polyhydric alcohols. Their patents list a very large number of useful compounds.

In concluding this survey of cyanogen-recovery methods, two methods may be mentioned which are unique though hardly practicable. Liebknecht [634] separated and recovered hydrocyanic acid from gases by absorption on active carbon, silica gel, or other highly porous material moistened with water. Wucherer [166] found that on cooling coke-oven gas to successively lower temperatures, advantageously under pressure, he removed water, ammonia, carbon dioxide, various light oil fractions, and finally obtained hydrogen cyanide in solid form at a temperature of $-100°$ C.

These newer methods for the recovery of hydrogen cyanide as such, particularly by scrubbing with water, make a knowledge of pertinent physicochemical data most desirable. Unfortunately, such data are not generally available in handbooks, but are widely scattered in the literature. For the benefit of those desiring a closer study of the problem the more recent contributions are here briefly summarized.

Partington and Carroll [635] determined the specific heats of hydrogen cyanide. Bredig and Teichmann [636] measured its critical temperature and pressure, its vapor pressures from $-15°$ C to the critical temperature, and its surface tension at 25° C. Perry and Porter [637] have given the vapor pressure of solid hydrogen cyanide from $-30°$ C to the triple point, and for the liquid from the triple point to $+27°$ C. They presented formulas for these data. Latent heats of sublimation, fusion, and evaporation were also given. Walker and

[630] Stavorinus, D., *Het Gas*, **42**, 183–7 (1923). Thau, A., *Gas- u. Wasserfach*, **73**, 827–9 (1930). TerNedden, W., *Brennstoff-Chem.*, **11**, 67–8 (1930).

[631] Felt, W. O., U. S. Pat. 1,237,767 (1917).

[632] Société anon. pour l'industrie chimique à Bâle, Fr. Pat. 717,999 (1931).

[633] Millar, R. W., and Groll, H. P. A., U. S. Pats. 2,086,731–2 (1937).

[634] Liebknecht, O., U. S. Pat. 1,605,897 (1926).

[635] Partington, J. R., and Carroll, J. F., *Phil. Mag.*, **49**, 1665–80 (1925).

[636] Bredig, G., and Teichmann, L., *Z. Elektrochem.*, **31**, 449–54 (1925).

[637] Perry, J. H., and Porter, F., *J. Am. Chem. Soc.*, **48**, 299–302 (1926).

Marvin [638] worked out a table by means of which the hydrogen cyanide content of a hydrogen cyanide-water mixture containing over 80 percent hydrogen cyanide can be determined with an accuracy of ±0.1 percent. Sinozaki, Hara, and Mitsukuri [639] determined the vapor pressures for solid hydrogen cyanide from −86 to −13.5° C, and for the liquid from −16 to +43° C. Shirado [640] reported the specific gravities of aqueous solutions of hydrocyanic acid over a wide range of concentrations, and Bredig and Shirado [641] have determined the vapor pressures and specific gravities of aqueous solutions ranging in concentration from 5 to 100 percent hydrogen cyanide. Schwarz [465] calculated and determined vapor pressures of hydrogen cyanide and its aqueous solutions at different temperatures and low concentrations, and determined the solubility of hydrogen cyanide in distilled water and in water saturated with fuel-oil gas or containing various acids or salts. Sinozaki and Hara [642] contributed determinations of the densities of gaseous and liquid hydrocyanic acid, the heats of vaporization and sublimation, and some thermodynamic calculations. Coates and Hartshorne [643] made a detailed study of the freezing points of hydrogen cyanide-water mixtures, finding only limited miscibility at low tempera-

tures. Fredenhagen [644] determined density, inner friction, dielectric constant, dipole moment, dissolving power, and dissociation power of hydrocyanic acid. He measured solubilities and conductivities of various salts in liquid hydrogen cyanide. Fredenhagen and Wellmann [645] calculated the distribution number of hydrogen cyanide and water over the two-component system H_2O-HCN at 18° C.

The small amount of hydrocyanic acid contained in coal carbonization gases and the restricted markets for cyanide products have always mitigated against its recovery. Small wonder that a surprising number of efforts were made either to convert it to ammonia or to destroy it completely. Most of these proposals are based on the fact that hydrogen cyanide is the nitrile of formic acid, and that therefore saponification with either alkali or acid will yield ammonia. Under proper conditions even water, or steam, is suitable for saponification.

As has already been pointed out in the ammonia section of this chapter, the formation of hydrogen cyanide in coking is suppressed by the presence of steam, as when wet coking coals are used. Dunnachie [142] converted those quantities of hydrogen cyanide which were formed in blast furnaces, coke ovens, gas producers, and the like by subjecting them outside of the gas-producing equipment to a treatment with steam. Collin [143] treated gases containing hydrogen cyanide, after the separation of ammonia, with steam and sulfuric acid in a special apparatus. Ammonium sulfate was thus produced. An alkaline hydrolysis is indicated by the findings of Foulis [519] that the cyanogen is converted

638 Walker, M., and Marvin, C. J., *Ind. Eng. Chem.*, 18, 139–42 (1926).

639 Sinozaki, H., Hara, R., and Mitsukuri, S., *Bull. Chem. Soc. Japan*, 1, 59–61 (1926); *Chem. Abs.*, 20, 2437 (1926).

640 Shirado, M., *Bull. Chem. Soc. Japan*, 2, 122–4 (1927); *Chem. Abs.*, 21, 2832 (1927).

641 Bredig, G., and Shirado, M., *Z. Elektrochem.*, 33, 209–11 (1927). Shirado, M., *Bull. Chem. Soc. Japan*, 2, 85–95 (1927); *Chem. Abs.*, 21, 2411 (1927).

642 Sinozaki, H., and Hara, R., *Tech. Repts. Tohoku Imp. Univ.*, 8, No. 3, 19–64 (1929); *Chem. Abs.*, 23, 4860 (1929).

643 Coates, J. E., and Hartshorne, N. H., *J. Chem. Soc.*, 1931, 657–65.

644 Fredenhagen, K., *Trans. Electrochem. Soc.*, 60, 153–63 (1931).

645 Fredenhagen, K., and Wellmann, M., *Z. physik. Chem.*, A162, 467–70 (1932).

to ammonia if the gas is passed through lime purifiers before entering the oxide boxes. This was verified by Hunt,[646] who made the same observation but considered the dilutions too great to warrant recovery. Sommer [647] made a splendid study of the problem, particularly as regards the development of a method of cyanogen conversion which could be adapted to coke-plant operation with a minimum of trouble and expenditure. He employed saponification with 60° Baumé sulfuric acid and had no difficulty in getting a 98.4 percent yield. In a number of tests he used diluents such as steam, carbon dioxide, and hydrogen and found that they impaired the yield somewhat. Temperatures of 70 to 100° C were found to be satisfactory. The principal reaction involved is the complete destruction of the hydrogen cyanide molecule according to the equation:

$$HCN + HOH = NH_3 + CO$$
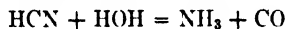
(no doubt involving the intermediate formation of formic acid), but Sommer observed as side reactions the formation of hydrogen:

$$HCOOH = CO_2 + H_2$$
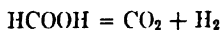
and even of some methane. For the practical application of his principle, Sommer proposed to use a modified Collin saturator with a built-in saponifier (shown in Fig. 13) in which hydrogen cyanide comes in intimate contact with hot 60° Baumé sulfuric acid. Sommer contemplated using his scheme for indirect ammonia plants, which do not handle the gas itself in the saturator but only the gases coming from the ammonia stills. Since the ordinary ammonia liquor worked up in such plants contains only a fraction of the total cyanogen

of the gas, Sommer suggested employing the O'Neill process,[511] in which the gas is scrubbed with ammonia concentrate from the ammonia stills, thereby removing all the cyanogen from the gas. It is doubtful that the Sommer process would be applicable to American practice, which largely
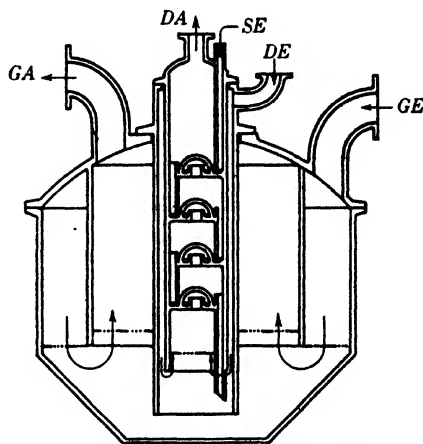
FIG. 13. Modified Collin saturator with built-in saponifier.[647]
GA—gas outlet.
GE—gas inlet.
DE—inlet of still vapors containing ammonia, carbon dioxide, hydrogen sulfide, and hydrogen cyanide.
DA—outlet of still vapors.
SE—inlet for sulfuric acid.

employs the semi-direct ammonia-recovery system.

In a number of gas-purification systems, also, hydrocyanic acid is eventually recovered in the form of ammonia. Thus Burkheiser [319] obtained it in his process as ammonium thiocyanate. This he converted to the calcium salt, which was converted to ammonia by an undisclosed process. He asserted that the yield of ammonia was increased in this manner by about 10 percent. Reichel,[648] in his report on the Burk-

646 Hunt, C., *J. Gas Lighting*, **69**, 1055 (1897).
647 Sommer, F., *Stahl u. Eisen*, **41**, 852–9 (1921).

648 Reichel, J., *ibid.*, **33**, 982–7, 1028–30 (1913).

heiser process, said the same thing, but gave little information as to the conversion process employed except that the calcium thiocyanate was "heated, or oxidized or reduced." The process Burkheiser had in mind is indicated by some of his patents,[649] according to which the thiocyanates were added to the coal to be coked in the ovens, or simply heated with lime. Thiocyanate solutions may be treated with nascent oxidizing or reducing substances such as hydrogen peroxide, sulfur dioxide, or nascent hydrogen. Overdick,[355, 357] in his process for the simultaneous recovery of ammonia and hydrogen sulfide from the gas, recovered the hydrogen cyanide in the form of a strong solution of ammonium thiocyanate, which was decomposed with sulfuric acid at 100 to 180° C to form ammonium sulfate. Hansen[366] in his CAS process, described in detail in the ammonia section of this chapter, also recovered hydrogen cyanide as ammonia, together with the hydrogen sulfide and ammonia of the gas. He first converted it to thiocyanate, which was then hydrolyzed under pressure in an aqueous solution containing polythionic acids, according to the equation

$$NH_4SCN + 2H_2O = 2NH_3 + H_2S + CO_2$$
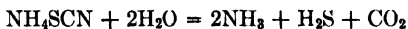
The hydrolysis of ammonium thiocyanate to ammonia has become an important problem for the industry since it fits so nicely into the general arrangement of the normal coke plant. Reference may therefore be made to a number of papers and patents dealing with this subject.[360, 361, 650]

Catalytic conversion in a practical man-

ner was achieved by Bähr[370] in his ammonia-cyanogen-sulfur recovery process, which has been outlined in detail in the ammonia section of this chapter. Carpenter and Linder[651] first observed the vapor-phase hydrolysis of hydrogen cyanide to ammonia when they noted the ammonia in the exit gases from a Claus kiln, in which saturator-waste gases (indirect process) were oxidized to sulfur. They attributed it to the interaction of hydrocyanic acid with the steam produced by the oxidation of the hydrogen sulfide. To verify their belief, they passed hydrogen cyanide, mixed with carbon dioxide and steam, or carbon dioxide, hydrogen sulfide, and steam, over broken brick at 300 to 600° C, and found conversion to ammonia and carbon monoxide to take place. In a later contribution,[652] the authors studied this reaction very much in detail, using broken brick, iron oxide, and Weldon mud as catalytic agents, with or without the addition of carbon dioxide, hydrogen sulfide, and air to the hydrogen cyanide-steam mixture. An ammonia yield of 96.5 percent was easily obtained at 280° C over iron oxide. Except when they used Weldon mud, which exerts a powerful oxidizing action, they observed practically no decomposition to free nitrogen at temperatures up to 625° C. The reactions involved are:

$$HCN + H_2O = NH_3 + CO$$
$$CO + H_2O = CO_2 + H_2$$
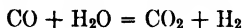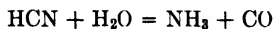
Schreiber[653] heated a number of nitrogenous materials in mixture with hydrated iron oxide to 350° C and obtained 46 to 74 percent of the nitrogen content as ammo-

[649] Burkheiser, K., Brit. Pats. 15,742, 15,972 (1912).

[650] Williams, P. E., Brit. Pat. 2,841 (1914). South Metropolitan Gas Co., Ger. Pat. 321,661 (1914). Evans, E. V., U. S. Pat. 1,148,368 (1915). Gluud, W., Schneider, G., and Schönfelder, R., *Ber. Ges. Kohlentech.*, **1**, 186–94 (1923).

[651] Carpenter, R. F., and Linder, S. E., *J. Soc. Chem. Ind.*, **22**, 457–65 (1903), **23**, 577–91 (1904).

[652] Carpenter, R. F., and Linder, S. E., *ibid.*, **24**, 68–71 (1905).

[653] Schreiber, F., *Chem.-Ztg.*, **35**, 943 (1911).

nia. Pyridine was one of the compounds used. By conducting coke-oven gas through a tube charged with hydrated iron oxide and heated to 350° C, all the nitrogen compounds were converted to ammonia. In an elaboration on this work, Schreiber[654] passed coke-oven gas, which contained 16 grains hydrogen cyanide per 100 cubic feet and from which the ammonia had been carefully removed, over ferrous or ferric oxide at 300° C; he found the resulting gas to contain 19 and 13 grains ammonia, so that besides the hydrogen cyanide other nitrogen compounds, e.g., pyridine, must have been decomposed.

Burkheiser; in his early gas-purification process, revivified the iron oxide by roasting it carefully at low temperatures. According to Reichel,[648] ammonia was always obtained in this roasting stage, a result which could be attributed only to conversion of the cyanogen taken out of the gas. Halvorsen[144] obtained a 99 percent conversion of hydrogen cyanide to ammonia when he passed a mixture of hydrogen cyanide, hydrogen, and some air over a catalyst of iron and chromium oxides at 400° C.

The last resort for the removal of hydrocyanic acid from gas is its destruction without recovery of any values. This has rarely been employed but bears further investigation inasmuch as the poor return for ammonia and lack of markets for cyanogen compounds would make this alternative attractive whenever it is deemed advisable to rid the gas of an undesirable constituent. Kaysser[655] suggested destroying it by permanganate wherever it exerts its destructive influence, as in gas holders and meters. A more practical aspect of the problem is presented in the disposal of ammonia-still effluents, which contain sizable quantities of thiocyanates. One method of disposing of such still waste is to destroy its harmful components by bacterial action. In so doing, the thiocyanate is oxidized by certain mixtures of bacteria, a large part of its nitrogen content appearing as nitrate. A number of references [387, 656] illustrate the principles involved.

As has been shown above, cyanogen is recovered from coal-distillation gases almost exclusively in the form of prussiates, thiocyanates, and ammonia. As the utilization of these compounds is usually left to chemical companies, literature on this subject will, therefore, not be reviewed in this chapter. However, it may be pointed out that the greatest efforts have probably been expended on finding processes for the conversion of prussiates and thiocyanates to cyanides and hydrocyanic acid. The older literature is splendidly abstracted by Williams,[417] Bertelsmann,[441] and Köhler.[495] Some of the more recent advances in the art are taken care of by Gluud and Jacobson[12] and by the *Berichte der Gesellschaft für Kohlentechnik.*[657] Still more recent patents are listed here.[658]

[654] Schreiber, F., *Z. angew. Chem.*, **25**, 2289–96 (1912).

[655] Kaysser, O., Ger. Pats. 198,238 (1907), 218,949 (1909).

[656] Fowler, G. J., Arden, E., and Lockett, W. T., *J. Soc. Chem. Ind.*, **30**, 174–9 (1911). Fowler, G. J., and Holton, A. L., *ibid.*, **30**, 180–1 (1911). Fowler, G. J., and Shepard, S. W., *ibid.*, **30**, 181–4 (1911). Institution of Gas Engineers, *Gas World*, **97**, 400–3, 433–5 (1932).

[657] *Ber. Ges. Kohlentech.*, **1**, 186–94 (1923), **1**, 325–36 (1924), **2**, 26–9, 55–68, 310–47 (1926), **3**, 385–419 (1931), **4**, 35–50 (1931), **4**, 305–9 (1933).

[658] Bergwerksverband zur - Verwertung von Schutzrechten der Kohlentechnik G.m.b.H., Ger. Pats. 488,271 (1924), 489,182 (1925). Van der Meulen, J. H., Ger. Pat. 449,730 (1928). Gluud, W., and Keller, K., Ger. Pats. 530,821 (1929), 576,531 (1933). Gluud, W., and Dieckmann, C., Ger. Pat. 526,716 (1930). Sulman, H. L., and Picard, H. F. K., Brit. Pat. 394,004 (1933). Ges. für Kohlentechnik m.b.H., Brit. Pat. 399,718 (1933) ; Fr. Pat. 752,296 (1933). Keller, K.,

DETERMINATION OF HYDROCYANIC ACID

Analytical procedures for the determination of hydrocyanic acid in coal-distillation gases, of simple and complex cyanides and thiocyanates obtained by the various cyanogen-recovery systems described above, and of the cyanogen compounds contained in ammonia liquor are extremely numerous. Owing to the great difficulty of the chemistry of cyanogen compounds, the publications are often contradictory, the older ones especially so. Feld [491] deserves the credit of having made the first comprehensive study of the various problems involved, and his methods have remained useful to this very day. Details of procedure are available in several textbooks. [12, 429, 430, 441, 495, 659] For the benefit of those desiring more information, a large number of publications have been arranged in five general groups; they should be consulted. Naturally, a considerable amount of overlapping must be expected since many papers could have been classified in several of these groups.

Group 1. Determination of hydrogen cyanide in gases. [474, 479, 492, 660]

U. S. Pat. 1,931,441 (1934). Van Seters, A. W., U. S. Pat. 2,035,030 (1936).

[659] American Gas Association, *Gas Chemists' Handbook,* Am. Gas Assoc., New York, 1929, 795 pp.

[660] Lee, J. W., *J. Gas Lighting,* **105,** 854 (1909). Mueller, M. E., *Progressive Age,* **28,** 1101–2 (1911); *Chem. Abs.,* **5,** 1833 (1911). Sell, G. E., *Ind. Eng. Chem.,* **18,** 142–3 (1926). Sell, G. E., Skelly, J. S., and Heiligman, H. A., *Gas Age-Record,* **60,** 179–80, 223–4, 259–60 (1927). Perna, F., *Plyn a Voda,* **8,** 139 (1928); *Paliva a Topeni,* **10** (1929); *Chem. Abs.,* **23,** 2552 (1929). Pieters, H. A. J., and Penners, K., *Het Gas,* **52,** 382 (1932), **55,** 402–4 (1935). Voituret, K., *Brennstoff-Chem.,* **13,** 264–5 (1932). Klempt, W., and Riese, W., *ibid.,* **14,** 21–5 (1933). Brender à Brandis, G. A., and Bohlken, S. F., *Het Gas,* **53,** 194–200 (1933). Boye, E., *Chem.-Ztg.,* **60,** 508–9 (1936). Eymann, C., *Gas- u. Wasserfach,* **81,** 484–8 (1938), **83,** 51–5 (1940); *Glückauf,* **76,** 586–9 (1940).

Group 2. Determination of hydrogen cyanide and simple cyanides in solution. [661]

Group 3. Determination of complex cyanides and thiocyanates. [436, 488, 491, 531, 555, 662]

[661] Grossmann, H., and Hölter, L., *Chem.-Ztg.,* **34,** 181 (1910). Schramm, Q., *J. Gasbeleucht.,* **56,** 389–91 (1913). Votoček, E., *Chem.-Ztg.,* **42,** 257–60, 271–2 (1918); *J. Chem. Soc.,* **114,** 11, 272 (1918). Lavialle, P., and Varenne, L., *J. pharm. chim.,* **17,** 97–102 (1918). Lang, R., *Z. anorg. allgem. Chem.,* **142,** 280–98 (1925). Votoček, E., and Kotrba, J., *Collection Czechoslov. Chem. Commun.,* **1,** 165–72 (1929); *Chimie & Industrie,* Special No. 164 (1929); *Chem. Abs.,* **23,** 3640 (1929). Rosenthaler, L., *Pharm. Acta Helv.,* **7,** 45–8 (1932); *Chem. Abs.,* **26,** 4556 (1932). Pagel, H. A., and Carlson, W., *J. Am. Chem. Soc.,* **54,** 4487–9 (1932). Morris, S., and Lilly, V. G., *Ind. Eng. Chem., Anal. Ed.,* **5,** 407–8 (1933).

[662] Knublauch, O., *J. Gasbeleucht.,* **32,** 450–9, 493–500 (1889). Gasch, R., *ibid.,* **32,** 966–71 (1889). Moldenhauer, C., and Leybold, W., *ibid.,* **32,** 155–8 (1889). Lubberger, H., *ibid.,* **41,** 124–6 (1898). Nauss, A. O., *ibid.,* **43,** 696–7 (1900). Bernheimer, O., and Schiff, F., *Chem.-Ztg.,* **26,** 227–8 (1902). Lührig, H., *ibid.,* **26,** 1039–41 (1902). Witzeck, R., *J. Gasbeleucht.,* **47,** 545–7 (1904). Colman, H. G., *Analyst,* **33,** 261–72 (1908), **35,** 295–306 (1910). Skirrow, F. W., *J. Soc. Chem. Ind.,* **29,** 319–23 (1910). Williams, H. E., *ibid.,* **31,** 468–71 (1912). Ronnet, L., *Ann. chim. anal.,* **16,** 366–7 (1912); *Chem. Abs.,* **6,** 50 (1912). Knublauch, O., *J. Gasbeleucht.,* **55,** 713–8 (1913); *Z. angew. Chem.,* Aufsatz, **26,** 425–31 (1913); *J. Gas Lighting,* **123,** 370–1 (1913). Myhill, A. R., *Gas World,* **60,** 387–9 (1914). Knapman, F. G. W., and Randall, E. L., *Chem. News,* **113,** 265–6 (1916). Randall, E. L., *J. Gas Lighting,* **133,** 581 (1916). Müller, A., *Chem.-Ztg.,* **42,** 457 (1918). Colman, H. G., and Yeoman, E. W., *J. Gasbeleucht.,* **145,** 68–9, 112–3, 169–70 (1919). Kolthoff, I. M., and van der Heyde, R., *Pharm. Weekblad,* **56,** 1565–8 (1919); *Chem. Abs.,* **14,** 504 (1920). Müller, E., and Lauterbach, H., *Z. anal. Chem.,* **61,** 398–403 (1922). Bellucci, I., and Ricca, B., *Atti congr. naz. chim. pura applicata,* **1923,** 476–82; *Chem. Abs.,* **18,** 3334 (1924). Cumming, W. M., *J. Chem. Soc.,* **125,** 240–3 (1924). Feigl, F., and Schummer, O., *Z. anal. Chem.,* **64,** 249–55 (1924). Lang, R., *Z. anorg. allgem. Chem.,* **138,** 271–7 (1924); *Z. anal. Chem.,* **67,** 1–15 (1925). Cumming, W. M., and Good, W., *J. Chem. Soc.,* **1926,** 1924–8. Kolthoff, I. M., and Vleeschhouwer, J., *Rec. trav. chim.,* **45,** 923–7 (1926). Bicskei, J., *Z. anorg. allgem. Chem.,* **160,** 271–2 (1927). Anon., *Chemistry & Indus-*

Group 4. Determination of cyanogen compounds in gas liquors.[663]

Group 5. Color reactions, semi-quantitative and qualitative determinations.[664, 665]

RECOVERY AND UTILIZATION OF PYRIDINE FROM GASES

As has already been stated, the term pyridine is commonly understood to em-

try, **47,** 1308–10 (1928). Knop, J., *Z. anal. Chem.,* **77,** 111–25 (1929). Schwicker, A., *ibid.* **77,** 161–9 (1929). Brender à Brandis, G. A., and Bohlken, S. F., *Het Gas,* **53,** 353–7 (1933). Willard, H. H., and Young, P., *J. Am. Chem. Soc.,* **55,** 3260–9 (1933). Boye, E., *Chem.-Ztg.,* **60,** 757 (1936).

663 Weisser, F., *Chem.-Ztg.,* **36,** 1285–7 (1913). *55th Ann. Rept. Alkali Works* (1918), pp. 53–74; *Chem. Abs.,* **14,** 825 (1920). Spielmann, P. E., and Wood, H., *J. Soc. Chem. Ind.,* **38,** 43–5T, 369–70T (1919). Shaw, J. A., *J. Ind. Eng. Chem.,* **12,** 676–7 (1920). Travers, A., and Avenet, *Compt. rend.,* **190,** 1015–6, 1128–9 (1930), **192,** 52–3 (1931).

664 Spacu, G., *Bul. Soc. Stiinte Cluj,* **1,** 284–91, 302–5 (1922); *Chem. Abs.,* **17,** 1772 (1923).

665 Browning, P. E., and Palmer, H. E., *Am. J. Sci.,* **23,** 448–50 (1907); *Z. anorg. allgem. Chem.,* **54,** 315–8 (1908). Lockemann, G., *Ber.,* **43,** 2127 (1911). Barnebey, O. L., *J. Am. Chem. Soc.,* **36,** 1092–3 (1914). Feigl, F., *Chem.-Ztg.,* **38,** 1265 (1914). Kolthoff, I. M., *Pharm. Weekblad,* **54,** 1157–71 (1917); *Chem. Abs.,* **12,** 30 (1918). Jennesseaux, L., *J. pharm. chim.,* **19,** 363–4 (1919); *Chem. Abs.,* **13,** 2494 (1919); *Ann. chim. anal. appl.,* **1,** 15–20 (1919); *Chem. Abs.,* **14,** 710 (1920). Chelle, L., *Bull. soc. pharm. Bordeaux,* **1919,** 70; *J. pharm. chim.,* **19,** 361 (1919); *Chem. Abs.,* **13,** 2494 (1919). Moir, J., *J. S. African Assoc. Anal. Chem.,* **3,** 16 (1920); *Chem. Abs.,* **15,** 1673 (1921). Sundberg, T., *Svensk Kem. Tids.,* **33,** 112–3 (1921); *Chem. Abs.,* **15,** 3431 (1921). Peset, J., and Aguilar, J., *Arch. med. legal,* **1,** 18–21 (1922); *Chem. Abs.,* **17,** 3149 (1923). Buchanan, G. H., *Ind. Eng. Chem.,* **15,** 637–40 (1923). Neureiter, Von F., *Deut. Z. ges. gerichtl. Med.,* **2,** 313–7 (1923); *Chem. Abs.,* **18,** 1627 (1924). Denigès, G., *Mikrochemie,* **4,** 149–54 (1926). Banerjee, P. C., *J. Indian Chem. Soc.,* **6,** 259–62 (1929); *Chem. Abs.,* **23,** 4907 (1929). Guglialmelli, L., and Ruiz, C., *Anales asoc. quim. argentina,* **17,** 189–208 (1929); *Chem. Abs.,* **24,** 1057 (1930). Pavlinovi, A. V., and Bakh, T. N., *Ukrain. Khem. Zhur.,* **5,** 233–4 (1930); *Chem. Abs.,* **25,** 2076 (1931). La Rosa, L., *Chim. ind. agr. biol.,* **9,** 90 (1933); *Chem. Abs.,* **27,** 2907 (1933).

brace a multitude of nitrogenous materials, generally of basic nature and predominantly of heterocyclic structure. The quantity produced in carbonizing coal is very small, much smaller than that of ammonia or cyanogen. Moreover, on account of their widely varying boiling points and their solubility in water and in oils, the pyridine bases are divided between the tar and the gas stream, making the quantity contained in each even smaller. Figures on the production per ton of coal have already been given, but in this section the recovery of values from the gaseous phase will be discussed, and the few available data on its pyridine contents will be presented.

Klempt and Röber,[83] in a very excellent paper on the recovery of pyridine from ammonia saturator exhaust in the indirect process, stated that the tar-free gas contains from 5 to 8 grains of bases per 100 cubic feet. Wald [666] recovered 10 to 14 grains per 100 cubic feet of gas, and, though Meredith [667] using the Schutt process obtained only 5 grains per 100 cubic feet, he stated that the gas entering the saturator contained 20 to 30 grains per 100 cubic feet. Thus a recovery between 5 and 15 grains from coke-oven gas may normally be expected. These figures will be influenced by a large number of factors, such as the kind of coal carbonized, kind and temperatures of the ovens, and kind of ammonia-recovery system. Where straight high-volatile coals are coked the yield is usually from two to three times higher than when coals or mixtures of lower volatile-matter content are coked. However, publications on this whole subject are very few and sadly lacking in de-

666 Wald, M. D., *Iron Steel Engr.,* **17,** 55–8 (1940).

667 Meredith, H. J., *Proc. Am. Gas Assoc.,* **1941,** 656–7. Schutt, J. W., U. S. Pat. 2,811,134 (1942).

tail, and a proper correlation of the factors mentioned above with the yields obtained has never been attempted. This certainly is virgin ground and a proper subject for searching study.

Unlike cyanogen, pyridine is not known to exert any harmful effects either on the equipment of the byproduct plant or on the gas-distribution system. However, it does give to ammonium sulfate a disagreeable odor, becomes obnoxious to the workmen if the sulfate is neutralized, and definitely promotes acidity and caking if left in the salt. Macleod, Chapman, and Wilson [668] have contended that the caking of ammonium sulfate is roughly proportional to the quantity of pyridine sulfate adhering to the crystal surfaces, and that as little as 0.001 percent has a very considerable effect. Nolte and Kramer,[669] in their specifications for acceptable ammonium sulfate, gave 0.05 percent as the upper limit for pyridine content. Further information on this subject has already been given in the ammonia section.

It is thus apparent that pyridine recovery would be quite desirable, but the intangible benefits derived therefrom would be too insignificant to prompt plant managers to install recovery equipment, and any proposed scheme must, therefore, stand on its own feet and pay for itself in dollars and cents. This was not possible in the past, when the supply of pyridine easily and cheaply obtainable from tar was more than adequate to fill the needs of industry. Beginning in the late '30's, however, the picture changed considerably. New uses have come to the fore, such as the preparation of pharmaceuticals and textile auxiliaries, which require

[668] Macleod, J., Chapman, C., and Wilson, T. A., *Gas J.*, **178**, 291–4 (1927).
[669] Nolte, A. G., and Kramer, W. A., *Water Works Eng.*, **85**, 1540 (1982).

greater quantities than can be furnished by the tar distillers, and a lucrative field is thus opened up for the coke plants.

Before taking up methods of recovering pyridine from gas it may be well to find out just how the pyridine bases are distributed in the gas. Comparatively little is known on this subject, and only recently have investigators endeavored to shed some light on it. Klempt and Röber [83] found for an indirect plant that about 40 percent of the pyridine in the crude gas coming from the ovens is separated with the tar, while 60 percent passes on with the gas and is found in the ammonia liquor and in the light oil. For a plant producing 9,890,000 cubic feet of gas the authors found in the crude gas 138.2 pounds of pyridine bases, distributed as shown in Table **XXIX**. Of

TABLE XXIX

DISTRIBUTION OF PYRIDINE BASES IN THE GAS FROM COKE OVENS [83]

Gas	Pyridine Bases
	pounds per 9,890,000 cubic feet
From ovens	138.2
After coolers	56.6
After ammonia scrubbers	7.9
After light oil scrubbers	2.71

the 81.6 pounds removed in the coolers, 48.5 pounds were contained in the tar and 33.1 pounds in the liquor. The latter quantity combined with the 48.5 pounds washed out in the ammonia scrubbers gave a total of 81.6 pounds entering the ammonia house with the ammonia liquors. Taking this amount as 100 percent, the distribution shown in Table **XXX** was obtained in the ammonia house.

Meredith [667] reported the distribution of pyridine for a semi-direct coke plant shown in Table **XXXI**. It is obvious from these tables that recovery of pyridine from

TABLE XXX

DISTRIBUTION OF PYRIDINE BASES IN THE AMMONIA HOUSE [83]

	Percent
Loss in still waste	11.0
Remained in saturator	4.5
Removed with sulfate	1.2
Vent gas from saturator	82.0

TABLE XXXI

DISTRIBUTION OF TAR BASES (PYRIDINE EQUIVALENT) FOR A SEMI-DIRECT COKE PLANT [667]

Gas entering the saturators	20 to 30 grains per 100 cubic feet
Gas leaving the saturators	10 to 15 grains per 100 cubic feet
Saturator liquor	40 to 50 grams per liter
Gas after the final coolers	0
Still waste	Trace
Ammonium sulfate	0.07 to 0.18 percent
Gas liquors	0.2 to 0.4 gram per liter

coal gas is most feasible somewhere in the ammonia house, depending on the type of ammonia-recovery system used.

The ammonia liquor itself contains too little pyridine to warrant a direct recovery. According to Klempt and Röber,[83] ammonia liquor of an indirect coke plant contained 0.148 gram of pyridine per liter, and liquor from a semi-direct plant, according to the above table by Meredith, contains from 0.2 to 0.4 gram per liter. In some cases, where liquor volume is very small, large amounts may be expected. Thus Széki and Romwalter [670] reported for a liquor from the low-temperature carbonization of a Bohemian brown coal a pyridine content of 8.85 grams per liter. Such high concentrations are rare and without practical consequence. For this reason, recovery from ammonia liquor has not been

practiced, though Shadbolt [671] proposed distilling the liquor in the presence of solvent oils such as gasoline, benzol, paraffin, naphtha, or creosote to facilitate the recovery of byproducts like pyridine.

The ammonia still waste contains even less pyridine (only 0.0123 gram per liter according to Klempt and Röber),[83] yet its recovery has been attempted by Knapp [672] in conjunction with a proposal for the removal of phenol. He suggested putting the still waste in contact with a vaporous absorbing medium such as benzol, in a continuous cyclical process. The liquid benzol containing pyridine and phenol was then to be treated with sulfuric acid to remove the pyridine.

Much better prospects are offered in the operation of the ammonia saturator, because in either the direct or the indirect ammonia process almost all the pyridine contained in the gas must pass through the saturator. Offhand one would assume that owing to its basic nature pyridine would be retained by the saturator acid as completely as ammonia. Such an assumption is incorrect, however, because pyridine sulfate dissociates readily, particularly at the relatively high temperatures and the low acid concentrations at which the average saturator is run. Gluud and Schneider [673] found this out when they attempted to recover pyridine from two old saturator baths in which they thought it had accumulated. Surprisingly, they found only 1.47 and 1.83 percent pyridine besides 5.15 and 7.27 percent free sulfuric acid. Laboratory tests, in which aqueous, acid pyridine sulfate solutions were distilled, confirmed the suspicion that pyridine sulfate is stable

670 Széki, J., and Romwalter, A., *Roy. Hung. Palatin-Joseph Univ. Tech. Econ. Sci., Pub. Dept. Mining Met.*, 8, 116–26 (1936) ; *Chem. Abs.*, 32, 3124 (1938).

671 Shadbolt, S. M., and Chemical Engineering, and Wilton's Patent Furnace Co. Ltd., Brit. Pat. 276,393 (1926).

672 Knapp, W. R., U. S. Pat. 1,878,927 (1932).

673 Gluud, W., and Schneider, G., *Ber. Ges. Kohlentech.*, 1, 42–3 (1921).

only at low temperatures and dissociates at elevated temperatures. The authors expressed the opinion that the larger portion of the pyridine leaves the saturator with the gas, and that cold sulfuric acid would be necessary to recover it. Dodge and Rhodes [674] found between 2.5 and 7.5 percent pyridine in saturator liquors containing from 6 to 10 percent sulfuric acid, the lower figure appearing to be the more common one. Wald [666] noted that a saturator bath after 8 hours' operation would contain about 2 percent and after 3 days' operation about 5 percent pyridine. Klempt and Röber,[83] in their studies on the recovery of pyridine from the saturator vapors of an indirect ammonia plant, investigated the equilibrium conditions in the system pyridine sulfate-sulfuric acid-pyridine, adapting their test procedure to plant conditions. Since the waste gases from an indirect ammonia saturator contain a large proportion of steam and about 40 grains of pyridine per 100 cubic feet, the authors treated solutions containing about 18 percent pyridine and enough sulfuric acid to bind it, plus sulfuric acid excesses of 0, 10, 50, 100, 200, and 300 percent, with steam containing 40 grains of pyridine per 100 cubic feet. After having passed through the solutions the steam was condensed and the amount of unabsorbed pyridine was determined in the condensate. The results of their tests are given in Table XXXII. It will be seen from the table that, unless there is a sufficient excess of sulfuric acid to bind the pyridine as the bisulfate, there is no absorption. On the contrary, pyridine is given off by the solutions and carried away by the gas stream. An excess of 200 percent is necessary for a really good removal.

TABLE XXXII

PYRIDINESULFURIC ACID WITH 18 PERCENT PYRIDINE [83]

	Percent Excess of Sulfuric Acid					
	0	10	50	100	200	300
Temperature °C	Pyridine carried over by 100 cubic feet of vapors in grains					
70	240	65	13			
90	250		48		0.4	0.0
100				10	2.2	1.3
110			120	21	4.4	2.2

Credit for the first plant-scale recovery of pyridine from gas apparently goes to Dodge and Rhodes,[674, 675] who treated the saturator liquor of the direct or semi-direct ammonium sulfate process with ammonia in order to liberate the pyridine bases. Theirs is a batch process, in which the pyridine content of the saturator is allowed to build up until pyridine sulfate comes out with the ammonium sulfate, whereupon the saturator liquor is emptied into a lead-lined still in which it is treated with ammonia from the ammonia still. The heat of neutralization is sufficient to drive over the pyridine, together with some water. Addition of about 1 pound of solid ammonium sulfate per gallon of distillate causes separation into two layers, the upper of which is almost-dry pyridine. The sulfate solution contains in suspension solids, such as iron sulfide and iron-cyanogen compounds, which are removed by filtration before its return to the saturator. In a modification described in the second U. S. patent of the inventors, the pyridine bases are not distilled but extracted from the neutralized solution by means of organic liquids. This modification was apparently never practiced on a plant scale.

The most serious disadvantage of the Dodge and Rhodes process, as pointed out by Wald,[666] seems to have been the need

674 Dodge, F. E., and Rhodes, F. H., *Chem. & Met. Eng.*, **22**, 274–5 (1920) ; *Trans. Am. Inst. Chem. Engrs.*, **12**, 239–44 (1919).

675 Dodge, F. E., and Rhodes, F. H., U. S. Pats. 1,274,998–9, 1,275,000 (1918). Barrett Co., Brit. Pat. 122,397 (1918).

for a standby saturator, which few plants have available for such a purpose. It may have been the chief reason why this simple process was not adopted generally. The operation itself apparently was quite satisfactory.

Sperr and Brown [676] proposed to recover pyridine from saturator liquor by steam distillation, but no advantage can be seen in such a procedure over that of Dodge and Rhodes. Parrish [677] operated one saturator on the acid side with vapors from the free-ammonia still, and one on the alkaline side with vapors from the fixed-ammonia still. Salt produced in the first saturator was transferred to the second. There it was neutralized and thus freed of its pyridine content, which was recovered from the vapors escaping from it.

Wald [666] adapted the Dodge and Rhodes scheme to practical needs and made it into a continuous process. Instead of allowing the pyridine content of the saturator to build up, he withdrew some of the liquor continuously, 4 to 5 gallons per minute, and discharged it into a cooled tank in which it was neutralized with ammonia-still vapors. A crude pyridine separated from the neutral ammonium sulfate liquor and was removed continuously or intermittently. The pyridine-free sulfate solution returned continuously to the saturator without filtration. Inasmuch as the pyridine content of the saturator was thus maintained constant at about 1 percent, which is below the equilibrium concentration, a satisfactory removal from the gas stream should be assured in this process.

Schutt [667] cleverly combined the good features of the processes of Dodge and Rhodes, Sperr and Brown, and Wald, and

thus evolved a very workable and simple scheme. Liquor was removed from the drain tables at the rate of 1.5 gallons per minute and was then "steam-distilled" in a neutralizer with vapors from the ammonia stills. The effluent from the neutralizer was kept at a pH of 6 to 7 to prevent iron sulfide and iron-cyanogen compounds from separating out, and was returned to the saturator. The vapors from the neutralizer were dephlegmated so that they left at a temperature of 92 to 96° C and were then condensed to a liquor which separated into two layers, the upper one representing the pyridine bases and the lower one a strong solution of ammonium carbonate, which was discharged into the ammonia liquor system. Thus the special salting out employed by Dodge and Rhodes is avoided, but only if the ratio of ammonia to carbon dioxide in the dephlegmator vapors is such that a condensate sufficiently strong in ammonium carbonate is produced. The pyridine bases thus produced contain about 15 percent water. Figure 14 illustrates the process.

Klempt and Röber [83] worked out a process for the recovery of pyridine from the saturator operation of the indirect ammonia system which was largely used in Europe. It is based on their equilibrium studies reported above. Their problem was the utilization of the saturator vent gases, composed largely of steam, carbon dioxide, hydrogen sulfide, and hydrogen cyanide, in which they found 82 percent of the pyridine to be concentrated. Since pyridine is the only basic component of these gases, a simple scrubbing with sulfuric acid should be sufficient; but the acid concentration and temperature of operation should be such that there will be no substantial partial pressure of pyridine over the solution, and that the water tension will be about 1 atmosphere. In this manner sufficiently

[676] Sperr, F. W., Jr., and Brown, R. L., U. S. Pat. 1,414,441 (1922).

[677] South Metropolitan Gas Co. and Parrish, P., Brit. Pat. 176,977 (1921).
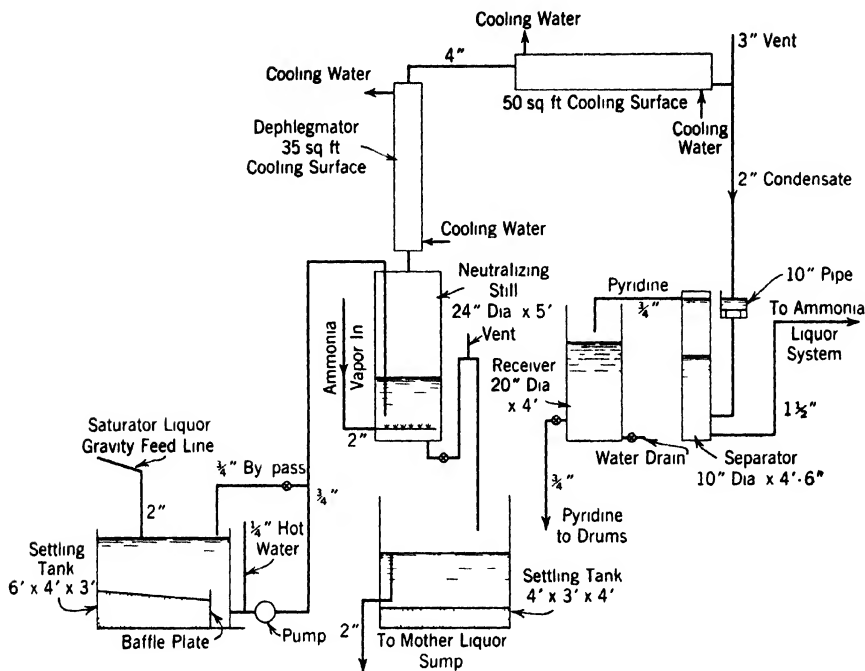
FIG. 14. Flow diagram of a plant for recovery of tar bases from saturator liquid.[667]

high pyridine concentrations should be obtainable. The process works as follows:

The hot saturator vent gases are passed at the temperature of 95 to 98° C through a trap, in which a small amount of steam is condensed, into a lead-lined saturator filled with 50 percent sulfuric acid. A steam jacket maintains the bath at a temperature at which steam is condensed only to such an extent that the continuously added concentrated sulfuric acid is diluted to 50 percent. This condition obtains if the bath is about 10 to 12° C hotter than the incoming gases. The pyridine-sulfuric acid thus obtained is discharged periodically or continuously, and is neutralized in stages by introducing ammonia. Close to the neutral point the weaker bases are precipitated, i.e., largely quinoline bases; on

further neutralization the stronger, lower-boiling bases of the pyridine group come out. A rough separation into three fractions is achieved by this simple expedient.

As long as there is a sufficient excess of sulfuric acid in the saturator a recovery of 90 percent of the bases contained in the vent gases presents no difficulty, but as soon as the bisulfate stage is reached the efficiency drops off. The acid solution sent to the neutralizer contains about 250 to 300 grams total pyridine bases per kilogram.

Fortunately, Klempt and Röber[88] also investigated the composition of the crude pyridine bases produced by their process, and their analysis at present furnishes the only clue to what bases are contained in coal gas. It is given in Fig. 15, together with the boiling curve.

The ammonia saturator so far has remained the only spot in the coke plant where pyridine recovery from gas is practicable, but some attention has also been paid to the light oil and the various prod-

production of coumarone and indene resins from solvent naphtha by a two-step acid wash, called attention to the fact that pyridine bases may be recovered from the first wash by neutralization with alkali.

No	Fractions	B.P.	%
1	Pyridine	115	69
2	α·Picoline	129	3
3	β·Picoline 2,6-Lutidine	143	3.5
4	γ·Picoline	145	1
5	2,4,6-Collidine	172	06
6	Aniline	184	4
7	Quinoline Bases	238	12

Up to 150°.- Close Fractionation Column
150-200°:- Widmer Column
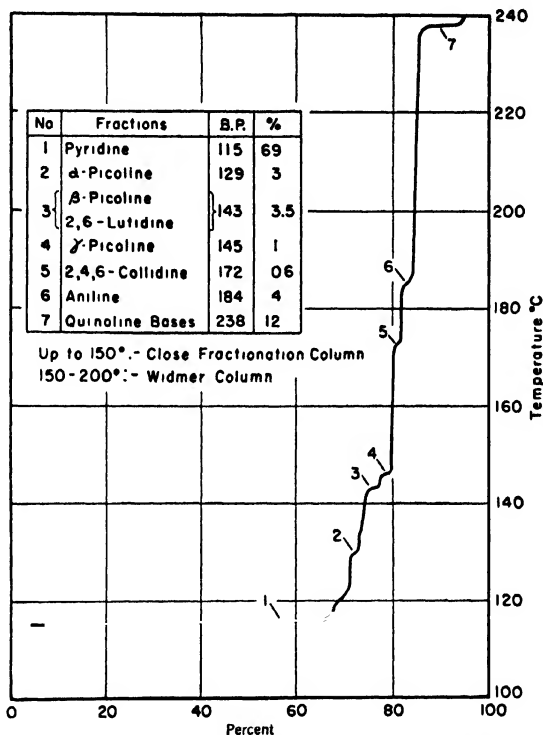
FIG. 15.   Distillation curve of crude pyridine bases.[a]

ucts obtained therefrom. It is natural that since the normal saturator operation lets the bases go through they would be found in subsequent processing steps. Their great solvent power and their miscibility with most organic compounds would lead us to suspect that they might be washed out together with the light oil, and that indeed happens.

Darrin,[678] in describing a process for the

Stephenson[679] dealt with the regeneration by heat treatment of acid sludge, obtained in the purification of benzene, and pointed out that 8 percent "pyridine oil" may be obtained from the acid distillate produced in the heat treatment.

Gluud and Schneider[680] carried out a

678 Darrin, M., U. S. Pat. 1,297,328 (1919).

679 Stephenson, G., Gas World, 74, No. 1907, Coking Sect., 19–20 (1921) ; Chem. Trade J., 68, 176 (1921).
680 Gluud, W., and Schneider, G., Ber. Ges. Kohlentech., 1, 93–111 (1921).

very thorough investigation of the pyridine content of crude light oil and its various fractions, and of the best means for its recovery. When they attempted to get a complete balance of the bases as distributed over the individual fractions, they found that only one-half the quantity ascertained for the crude light oil was contained in the oils distilled up to 180° C. The other half remained in the still residue. This strange phenomenon was explained by the assumption that pyridine bases and phenols form rather stable compounds which do not distil and are not decomposed up to at least 180° C. However, they are destroyed by caustic soda, and, if the recovery of all the bases is desired, the crude light oil should first be washed with caustic and then with acid. Such a procedure will be profitable only if there is a sufficient market for the higher bases, since a large percentage of them is recovered in this manner, together with the lower ones of the pyridine group.

Crude light oil, according to the authors, contains about 1.6 percent by weight of pyridine bases, but they are predominantly the higher-boiling ones: those which boil below 160° C and can be recovered without a preliminary caustic wash constitute only 0.35 percent of the crude light oil. A rough measure of the distribution of low- and high-boiling bases is given in the statement that bases from the light-oil fraction (b.p. 80 to 120° C) contain 9 parts low-boiling compounds for 2 parts high-boiling ones, and bases from the fraction 120 to 180° C contain 16 parts low-boiling for 17 parts high-boiling compounds. The ratio of high-boiling to low-boiling bases doubtless depends somewhat on the kind of wash oil used. German practice employs tar oils as wash oils, and this may explain the rather large quantity of high-boiling bases which the authors found. American practice should produce more low-boiling material.

Gluud and Schneider [680] advocated the use of 35 percent sulfuric acid for the washing step, in order to avoid resinification and emulsion troubles. If it is desired to produce chiefly low-boiling materials, advantage is taken of their greater basic strength. For instance, if the wash acid contains only one-third low-boiling and two-thirds high-boiling bases, it is used to wash a second batch of light oil; thereby some of the high-boiling bases are replaced by low-boiling ones, so that the acid now contains two-thirds low-boiling bases.

Pieters and Mannens [681] also recovered pyridine from crude light oil. They found that 16 tons of light oil yielded 34 kilograms of pyridine dissolved in dilute sulfuric acid at a concentration of 150 grams per liter and 50 kilograms phenol in a caustic solution containing 140 grams per liter. The acid consumption decreased 30 percent and the washing losses 35 percent.

The observation by Gluud and Schneider [680] that complexes of phenol with pyridine interfere in the recovery of pyridine is of great importance. Attention is therefore called to other papers on the same subject. Hatcher and Skirrow [682*] and Skirrow and Binmore [683] dealt exclusively with this topic; they came to the conclusion that phenols must be extracted from coal-tar oils by sodium hydroxide before pyridine can be recovered economically. Kulev [684] studied the nature of complexes of phenols with amines by determining the changes in electromotive force of their re-

681 Pieters, H. A. J., and Mannens, M. J., *Chem. Weekblad,* **26,** 286–90 (1929) ; *Chem. Abs.,* **23,** 3560 (1929).

682 Hatcher, W. H., and Skirrow, F. W., *J. Am. Chem. Soc.,* **39,** 1939–77 (1917).

683 Skirrow, F. W., and Binmore, T. V., *ibid.,* **40,** 1431–42 (1918).

684 Kulev, L. P., *J. Gen. Chem. (U.S.S.R.),* **5,** 1566–75 (1935) ; *Chem. Abs.,* **30,** 2183 (1936).

action with sodium. He found one complex to consist of one mole phenol and three moles pyridine. There is an indication that the complexes are of varying stability.

As illustrated by Fig. 15, the pyridine bases recoverable from coal-distillation gases comprise a mixture of a large number of compounds. Though many have been identified, and some have been separated from the mixture in reasonably pure form, the production of really pure individuals has proved to be a difficult task. The following papers and patents are devoted to the problems of dehydration and purification.

Downs [685] employed an azeotropic distillation for the removal of 15 percent water from a crude base mixture. He added enough benzol to give a weight ratio of benzol to water of 10.325 to 1. In this proportion, benzol and water form a binary mixture which boils constantly at about 69.5° C. Three fractions were taken off during the distillation. The first, up to 80° C, contained nearly all the water; a second, of boiling point 80 to 115° C, consisted of a little water, benzol, and a little pyridine, and the third fraction, above 115° C, was almost pure pyridine with its homologs.

Huff [686] separated the bulk of the water, together with pyridine, by a simple distillation and dehydrated the distillate with water-absorbing salts. The dehydrated distillate was returned to the still. In a modification, he proposed the use of volatile petroleum oils to aid in the distillation, a procedure similar to that of Downs.

Arndt and Nachtwey [687, 688] developed a unique process for the preparation of pure pyridine from a crude mixture, which is based on the observation that its perchlorate crystallizes exceedingly well and is rather sparingly soluble in water, whereas the perchlorates of its homologs are quite soluble. In this manner, pyridine can be separated from its homologs entirely selectively, a separation which cannot be effected by fractional distillation. Instead of using the costly free perchloric acid the process employed hydrochloric acid and sodium perchlorate. The precipitated pyridine perchlorate was filtered off, washed with perchloric acid or a saturated solution of ammonium perchlorate, and dried at 110 to 120° C. This product was subjected to a stream of dry ammonia gas while being cooled, and was thus decomposed to yield free pyridine. The treatment with ammonia was discontinued before the perchlorate had been decomposed completely; excess ammonia was removed by treatment with air at 60° C; and the pyridine was distilled in vacuo and dried with powdered potassium hydroxide. Pyridine prepared by this process from various crudes showed b.p.$_{739.5}$ 114.2° C, b.p.$_{755}$ 115° C, d_4^{20} 0.9819, d_4^{25} 0.9765, m.p. -39 to $-40°$ C. Such products are entirely free of ammonia, because anhydrous pyridine can be separated from ammonia, whereas in the presence of water separation is impossible. The authors also called attention to the precipitation of pyridine from an aqueous solution by means of cadmium chloride.

Wilkie and Shaw [689] separated pyridine and α-picoline by a careful fractional distillation. They found for pyridine b.p.$_{760}$ 115.3° C, d_4^{25} 0.9778, and for α-picoline b.p.$_{760}$ 128 to 128.6° C, d_4^{25} 0.9401. Madel and Fawcett [690] employed petroleum ether

[685] Downs, C. R., U. S. Pat. 1,290,124 (1919).
[686] Huff, W. J., U. S. Pat. 1,416,205 (1922).
[687] Arndt, F., and Nachtwey, P., Ber., 59B, 448–55 (1926).
[688] Arndt, F., and Nachtwey, P., Ger. Pat. 451,956 (1927).
[689] Wilkie, A. L., and Shaw, B. D., J. Soc. Chem Ind., 46, 469–71 (1927).
[690] Madel, W. R., and Fawcett, E. W., Brit. Pat. 355,213 (1930).

for the separation of bases from crude mixtures at low temperatures. Tartarini and Samaja[691] prepared pure pyridine, α-picoline, and isoquinoline by precipitation in the form of metal complexes. Pyridine, for instance, is precipitated by the addition of cupric perchlorate and cupric sulfate; α-picoline remains in solution. This compound is precipitated by silver nitrate and ammonium pyrosulfate, and obtained in pure form from the precipitate by distillation with caustic and sodium sulfite. Isoquinoline is purified by dissolving it in water, adding nickel sulfate and potassium thiocyanate, and neutralizing with sodium acetate. A precipitate separates which contains two moles of nickel thiocyanate for four moles of isoquinoline. Quinoline does not interefere. Schrauth[692] purified pyridine by heating the mixture to about 350° C in the presence of basic metal oxides, such as those of copper and calcium or of copper and lead. Goost and Lommel[693] refined commercial pyridine and its homologs by a treatment with compounds containing the group =NM or —NM, where M is an alkali or alkaline-earth metal. Thus, commercial pyridine may be heated to 100° C with 5 percent of sodium cyanamide, or stirred at normal temperatures with 3 to 5 percent of sodamide. The treatment is particularly useful as a preliminary to catalytic hydrogenation. Fisher[694] separated pyridine and homologs from aqueous solutions by extracting them with pseudocumene.

The field of isolating individual compounds from the crude mixture of pyridine bases in the form of complex metal salts is far from being preempted. In fact, there is every indication that attempts like those of Tartarini and Samaja[691] are the mere beginning of a very fruitful development, and it is suggested that researches of the industry for new methods of separation be directed along these lines. A wealth of information is available in the papers written on the legion of Werner complex salts which, if properly utilized, might well serve as the foundation of a number of practical processes. Heterocyclic bases, such as pyridine, have been used instead of ammonia with most of the better-known complex-building metals, such as copper, cobalt, nickel, and chromium; and it should not be too difficult to find a suitable combination which would allow the separation of a specific individuum from a mixture. The closely related heteropoly acids, such as phosphomolybdic acid and silicotungstic acid, should also prove useful for the direct precipitation of pyridine bases.

A number of analytical procedures are based on complex formation between pyridine bases and metal salts, and there is no reason why they could not be developed as technical processes. For instance, Spacu[694, 695] precipitated pyridine as a copper-thiocyanogen salt of the formula $CuPy_2(CNS)_2$ and found the reaction sensitive to 1 part in 2,000, and Mach and Sindlinger[696] used silicotungstic acid to separate pyridine from nicotine. Espinos, as well as Pavolini, used potassium iodobismuthate in determining pyridine in a crude mixture, and Tallantyre employed phosphotungstic acid and silicotungstic acid.[697] These examples may suffice to illustrate the possibilities outlined above.

691 Tartarini, G., and Samaja, T., *Ann. chim. applicata*, **23**, 351–6 (1933); *Chem. Abs.*, **27**, 5741 (1933).

692 Schrauth, W., U. S. Pat. 2,014,867 (1935).

693 Goost, T., and Lommel, W., Ger. Pat. 605,-228 (1934); U. S. Pat. 2,016,426 (1935).

694 Fisher, W. E., U. S. Pat. 2,058,435 (1936).

695 Spacu, G., *Bul. Soc. Stiinte Cluj*, **1**, 352–5 (1922); *Chem. Abs.*, **18**, 2300 (1924).

696 Mach, F., and Sindlinger, F., *Z. angew. Chem.*, **37**, 89–92 (1924).

697 Espinos, G., *Ann. méd. légale criminol. police sci.*, **7**, 213–21 (1927); *Chem. Abs.*, **22**,

One of the practical questions so often raised springs from present market conditions, which offer a comfortable outlet for pyridine, and for some of its close homologs, but not for others. It is the question of converting one group of bases into one or several others. Very little work has been done on this subject, or if it was done it was left unreported, only one reference being available. Meerwein, Schoeller, and Schwenk [698] passed pyridine bases and hydrogen over a catalyst composed of cerium chromate on pumice, at temperatures of 620 to 640° C. When technical picoline (b.p. 125 to 130° C is thus treated, 52 percent of the resulting product boils below 125° C.

Similarly scarce are data on physicochemical properties. Riley and Bailey,[699] who determined the vapor pressures of pyridine, α-picoline, piperidine, quinoline, and isoquinoline over a wide range, found them to conform with Dühring's rule. Pushin and Matavulj [700] measured the index of refraction of benzene-pyridine and benzene-quinoline mixtures of various concentrations at 16.5° C.

As a matter of interest, but not of practical value, it may be pointed out that if the pyridine bases are not recovered from the gas in some manner they may show up even in the oxide boxes. For instance, Williams [417] analyzed a spent oxide and found it to contain 0.77 percent pyridine sulfate and 1.20 percent iron-pyridine ferrocyanide.

The analysis of pyridine bases has evoked a great deal of interest, and a large number of publications have appeared on this subject. Some concern themselves only with the qualitative detection of one or the other base, but they might be developed into quantitative methods. They are listed here for study.

Group 1. Qualitative and microchemical methods, color reactions, precipitation in the form of insoluble salts, largely as metal complexes.[664, 680, 696, 697, 701]

Group 2. Quantitative volumetric methods, using a variety of indicators, some with destruction of ammonia by hypochlorite.[88, 92, 667, 678, 681, 688, 687, 702]

701 Ost, H., *J. prakt. Chem.*, **28**, 271–2 (1883). Kinzel, W., *Pharm. Zentralhalle*, **31**, 239–42 (1890). Delépine, M., and Sornet, R., *Bull. soc. chim.*, **9**, 706–10 (1911). Wöhlk, A., *Gas World*, **57**, 413 (1913). German Customs Board, *Chem.-Ztg.*, **37**, 1035 (1913). Malatesta, G., and Germain, A., *Boll. chim.-farm.*, **53**, 225 (1913); *Chem. Abs.*, **9**, 1020 (1915). Olin, H. L., *J. Soc. Chem. Ind.*, **37**, 41–3T (1918). Goris, A., and Larsonneau, A., *Bull. sci. pharmacol.*, **28**, 497–8 (1921); *Chem. Abs.*, **16**, 886 (1922). Rosenthaler, L., *Schweiz. Apoth. Ztg.*, **59**, 477–9 (1921); *Chem. Abs.*, **16**, 1129 (1922). Lehner, F., *Chem.-Ztg.*, **46**, 877 (1922). Cordier, V., *Monatsh.*, **43**, 525–36 (1923). Spacu, G., and Voicu, O., *Bul. Soc. Stiințe Cluj*, **2**, 89–96 (1925); *Chem. Abs.*, **19**, 2181 (1925). Kulikov, I., and Krestovosdvigenskaja, T., *Z. anal. Chem.*, **79**, 452–60 (1930). Brüning, A., and Schnetka, M., *Chem.-Ztg.*, **58**, 156–7 (1934). Schmidt, O., *Angew. Chem.*, **47**, 151–2 (1934). Barta, L., and Marschek, Z., *Biochem. Z.*, **293**, 118–20 (1937).

702 Schulze, K. E., *Ber.*, **20**, 3391 (1887). Milbauer, J., and Stanek, V., *Z. anal. Chem.*, **43**, 215–22 (1904). Houghton, A. C., *J. Ind. Eng. Chem.*, **1**, 698–700 (1909). Bayer, A., *J. Gasbeleucht.*, **55**, 513–4 (1912). Baessler, O., *ibid.*, **55**, 905–6 (1912). Prideaux, E. B., *Trans. Faraday Soc.*, **15**, 137–47 (1919). Nicolardot, P. N., and Baurier, H., *Chimie & Industrie*, **2**, 777–9 (1919). Lunge, G., *Chemische-Technische Untersuchungsmethoden*, J. Springer, Berlin, 1921, Vol. I, pp. 645–6. Rindin, F., *Am. Gas J.*, **119**, 200 (1923). Van Nieuwenburg, C. J., *Chem. Weekblad*, **27**, 143–6 (1930); *Chem. Abs.*, **24**, 5661 (1930). Rhodes, F. H., and Younger, K. R., *Ind. Eng. Chem., Anal. Ed.*, **5**, 302–4 (1933).

1172 (1928). Tallantyre, S. B., *J. Soc. Chem. Ind.*, **49**, 466–8T (1930). Pavolini, T., *Chim. ind. agr. biol.*, **6**, 272–4 (1931); *Chem. Abs.*, **25**, 5114 (1931).

698 Meerwein, H., Schoeller, W., and Schwenk, E., Ger. Pat. 529,628 (1930).

699 Riley, F. T., and Bailey, K. C., *Proc. Roy. Irish Acad.*, **38B**, 450–3 (1929); *Chem. Abs.*, **24**, 2349 (1930).

700 Pushin, N. A., and Matavulj, P. G., *Z. physik. Chem.*, **A162**, 415–8 (1932).

LIGHT OIL FROM COKE-OVEN GAS

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About 1 percent by volume of coke-oven gas can be profitably condensed in a variety of ways, which include: (*a*) scrubbing with high-boiling petroleum or creosote solvents; (*b*) adsorption in beds of granular active solids; (*c*) compression and cooling.

Freed from the recovery medium, the immediate product is a clear yellow-brown, sometimes evil-smelling oil and is known as crude coke-oven "light oil." The unrefined product is chiefly a complex mixture of hydrocarbons, but sulfur, oxygen, and nitrogen compounds are also present in small amounts. The precise nature of the light oil depends on the properties of the coal gas and is also profoundly influenced by the design of the recovery system. In general, the three principal benzene-ring aromatic hydrocarbons are predominant, and normal light oil from high-temperature coke-oven operations contains 55 to 70 percent benzene, 12 to 20 percent toluene, and 4 to 7 percent xylene (chiefly the meta form). The yield varies from 3 to 4 gallons of crude light oil per ton of coal carbonized.

Refining consists mainly of sulfuric acid washing followed by separation, through fractional distillation, of the individual homologs in varying degrees of purity. The different grades of benzols, toluols, xylols, and solvent naphthas so produced find wide application as fuels, solvents, and raw materials for organic syntheses. In the United States in 1941 the products of the light-oil industry had a value of $23,668,801.

Although comprising only 1 percent by volume of the coal gas, the light oil contributes about 5 percent of the heating value. The replacement cost of the difference in heat content of rich and lean gas is an important factor in considerations of the economics of light-oil recovery. Light oil is almost invariably recovered in coke-plant operations incidental to steel manufacture since a low price is set for the gas.

At coke ovens operated mainly to supply municipalities with residential gas, the conditions are quite different. The small average size of the establishment, the attractive price usually obtained for gas, and the high cost of a complete traditional refining plant have all contributed to establish the belief that light-oil recovery is unprofitable at gas plants. In recent years new techniques of light-oil recovery based on the manufacture of only partially refined motor fuels combined with shipment of the more valuable toluol and xylol constituents to central processing plants for refining have made comparatively low-cost-recovery installations possible.[1] This circumstance, coupled with the use of heavy oil for Btu replace-

[1] Van der Hoeven, B. J. C., *Proc. Am. Gas Assoc.,* 1940, 736–7.

ment and the trend towards higher prices for toluol and xylol, has resulted in considerable light-oil-plant construction at gasworks coke ovens. Also attractive to gasplant management is the concomitant substantially complete removal of naphthalene and gum formers from the gas and the decided decrease in total sulfur content.

Inasmuch as large quantities of light-oil products, particularly toluols, are needed in modern warfare, light-oil recovery was practiced without exception at all coke-oven plants in England [2] and Germany in 1940.

HISTORICAL

The exact date of the discovery of benzene in coal gas is unknown, but as early as 1881 coal gas produced at the Bradford Road Works of the Manchester (England) Gas Department was washed with creosote oil for the recovery of benzol.[3] In 1887, the first German light-oil-recovery plant was erected by Brunck at the Kaiserstuhl Colliery near Dortmund.[4]

In America, the birthplace of the industry was Syracuse, New York, where the Semet-Solvay Engineering Corporation built the first coke-oven battery in 1893 and subsequently installed a light-oil-recovery system in 1898.[5] Keeping pace with the chemical industry, growth in the pre-World War I years was steady but slow. In 1914, there were 14 light-oil plants having outputs with a total value of nearly $1,000,000. Operated all by one company, most of the units shipped a crude light oil to central plants for refining. From 500,000 to 700,000 gallons of toluol

2 *Gas World Year Book, Directory*, **1940**, p. 95.

3 Irwin, W., *J Soc Chem Ind.*, **44**, 92–4T (1925).

4 Thau, A, *Oel, Kohle, Erdoel, Teer*, **13**, 568–83 (1937).

5 Tiddy, W., and Miller, M. J., *Am. Gas J.*, **153**, No. 3, 7–10, 46 (1940).

was adequate to fill the needs of all chemical industry.

Reference to Fig. 1 shows the production of light oil derived from coke ovens alone. Except for the World War I period the amount of light oil derived from other sources has been insignificant. The great changes World War I produced are apparent. Picric acid, trinitrotoluol, and trinitroxylol were demanded in great amounts; as a result, the construction of plants for recovery of light oil was strongly stimulated. In 1915 the number of such plants had swelled to 30. Spot prices for toluol reached $7.00 a gallon: the average selling price for toluol in 1915 was $2.45 a gallon, in 1917, $2.85 a gallon. Light-oil-recovery plants were erected as rapidly as engineering facilities would permit; during this period the Koppers Company alone built a refining unit every 27 days, and by 1918 it had become general practice to carry out refining at the recovery plant. Almost any source of toluol could be profitably exploited: toluol was recovered at tar refineries, at petroleum cracking plants, and at more than 40 gasworks. These additional sources, although numerous, were relatively small, and during World War I more than three-fourths of the crude light oil used in munitions manufacture came from coke-oven operations. During this period, recovery efficiencies were low compared with modern practice. In 1915 and 1918, yields of 1.54 and 2.4 gallons of light oil per ton respectively were obtained as compared with 2.99 gallons per ton in 1938 and 1939.

These low yields were reflected in a high operating cost per gallon of light oil produced. Consequently, the return to a normal price structure at the end of the war forced the general abandonment of light-oil removal except at steel plants. This was particularly true of gas plants, and by 1922 the wartime number of 40 had decreased
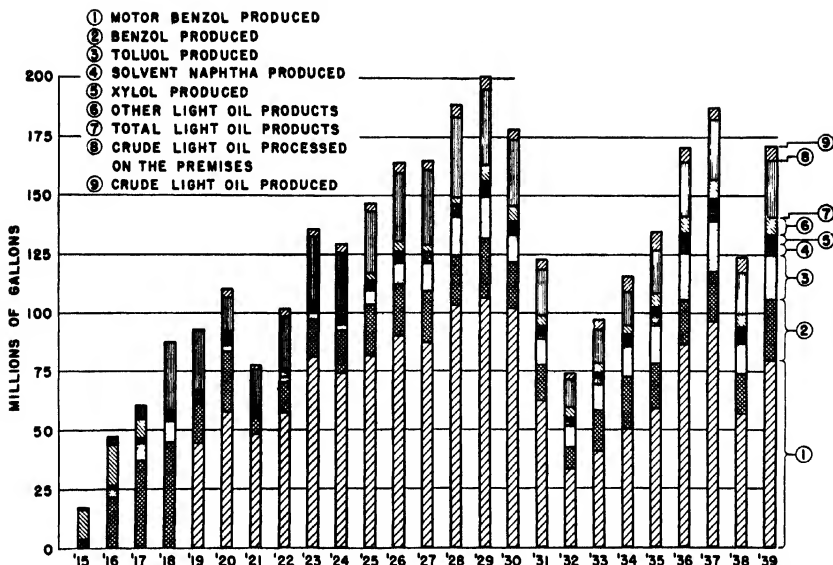
FIG. 1. Production of light oil and its products as obtained from publications of the U. S Bureau of Mines. (Omission of any classification in any specific year is due to lack of reliable figures. Prior to 1930, xylol was included in solvent naphtha)

to only 2. Producers of light oil turned to the then new automobile industry for markets, and much of the output was sold as motor fuel for blending with low-octane gasolines. The growth of the lacquer trade after 1925 gradually provided increasing outlets for toluol and naphthas as solvents. More recently, the rise and expansion of the synthetic chemical industry have absorbed increasing quantities of light-oil products as raw materials. In 1941, about 7 percent of the benzene produced was used in the synthetic resin industry, being converted to phenol for use in the manufacture of Nylon and of the phenol-formaldehyde type of resin and being alkylated as a step in the manufacture of styrene for synthetic rubber. Since the beginning of World War II, these requirements for benzene have increased and large amounts of

benzene have also been used in the manufacture of explosives and of aviation gasoline.

Since 1940, the figures for the distribution of light oil and its derivatives have been withheld in accordance with government policy. The latest figures, as given in Fig. 1 and Table I, show that the major portion of the benzene produced still was sold as motor benzene.

Inasmuch as premium gasolines can be sold at a price only slightly higher than that of regular gasolines the value of benzol sold as motor fuel is permanently established at not more than a few cents above gasoline prices. The relatively huge magnitude of the petroleum industry assures the coke-oven operator of an almost unlimited market at, unfortunately, a steadily decreasing income per unit. Reali-

TABLE I

COKE-OVEN LIGHT OIL AND ITS PRODUCTS

Production in Gallons *

	1935	1936	1937	1938	1939	1940
Crude light oil	133,696,803	170,234,202	187,054,346	123,559,610	170,963,199	215,213,667
Benzol, crude and refined	20,210,207	19,412,593	21,660,522	17,744,657	25,305,714	31,880,556
Motor benzol	58,379,910	85,672,953	95,526,695	56,349,589	79,607,150	101,140,079
Toluol, crude and refined	16,026,438	19,807,383	20,896,724	13,021,080	19,767,200	26,406,407
Solvent naphtha	3,992,338	5,189,232	5,725,918	3,706,258	4,788,836	5,220,979
Xylol	3,695,656	4,216,081	4,562,344	2,900,243	4,089,090	5,645,993
Other light-oil products	5,235,866	6,673,992	8,130,103	5,450,045	6,247,201	7,500,617
Total derived products	107,540,415	140,972,234	156,502,306	99,171,872	139,805,191	177,794,631
Refined on premises	126,688,359	163,990,960	182,030,795	117,248,545	163,947,167	207,272,848

* Data from *Minerals Year Books*, U. S. Dept. of the Interior.

zation of this apparently permanent long-time trend in motor-fuel prices gave impetus to a search for new uses for benzol, to investigations aimed at the extraction of new products from light oil, and the development of more efficient, and consequently cheaper, refinement techniques. A noteworthy example in the last category is the wide application in the United States of the "inhibitor process" originally developed in England by Hoffert and Claxton.[6] The restricted petroleum resources of Great Britain and Germany have focused attention on the prime desideratum of increasing motor-benzol yields. As described more fully in a later section, this was attained concurrently with a substantially cheaper plant design and greatly reduced operating costs.

THE COMPOSITION OF LIGHT OIL

The constitution of any particular light oil is a function of both the type and efficiency of the recovery process and the detailed nature of the coal gas involved. Theoretically, the cyclic absorption proc-

[6] Hoffert, W. H., and Claxton, G., *Motor Benzole; Its Production and Use*, The National Benzole Association, London, 2nd ed., 1938, 933 pp. An excellent, comprehensive treatise on practically all phases of light-oil recovery and utilization with special emphasis on motor-benzol manufacture.

ess, which is invariably used in this country with a petroleum oil, can be operated to produce a light oil containing all its components in the proportions in which they exist in the gas. Complete absorption would involve very high oil-to-gas ratios in the absorbing cycle, large energy consumption in the desorption step, and high investment costs for extra-large equipment. Ordinarily it is most feasible to operate so that substantially complete recovery of the toluol fraction is obtained and to allow the benzol and xylol extraction efficiency to suffer. Under these circumstances varying quantities of both the relatively low- and relatively high-boiling components escape removal from the gas while a significant quantity of the absorbent contaminates the light oil. Recovery efficiencies vary from plant to plant and at any one installation may vary widely with the seasons.

The composition of the light oil will also vary with the type of recovery system. Active carbon plants, which are not used in the United States but which find considerable application in Germany and Great Britain, produce a light oil containing much larger amounts of such low-boiling compounds as carbon disulfide, cyclopentadiene, the amylenes, hydrogen sulfide, and hydrogen cyanide than are present in the

light oil obtained by the cyclic absorption process.

It is readily apparent that the nature of any crude light oil is profoundly influenced by the previous history of the coal gas. The construction of the oven or retort, the detailed chemical and petrographic structure of the coal, the carbonization conditions, and the type of ammonia- and tar-recovery system all contribute to defining the constitution of the light oil. Low-temperature carbonization methods produce light oils containing more aliphatic, naphthenic, phenolic, and unsaturated compounds, with correspondingly smaller amounts of aromatic homologs, than ordinary high-temperature light oil.[7] This material is not readily serviceable as a raw material in the production of pure aromatic compounds by conventional refining procedures. Low-temperature light oil is of no commercial importance in the United States. Abroad, it is used as a motor fuel.

As would be expected, the type and mode of operation of the carbonization system distinctly influences the composition of the light oil. In general, light oils produced in vertical, inclined, or horizontal gas retorts contain larger quantities of unsaturated and saturated nonaromatic hydrocarbons than ordinary coke-oven light oils.[8] Since the great bulk of American light oil is produced incidentally to the operation of the large, horizontal chamber coke oven of the familiar Koppers or Becker type, the detailed discussion will be confined to high-temperature light oils from this and similar sources.

Yields and compositions of light oils from different coals do not correlate well with any of the defining functions of the usual coal classification schemes. Fieldner and Davis[9] found the yield to vary with the rank[10] of the coal in the low- and medium-volatile groups, whereas in the high-volatile A, B, C classes the average yield is substantially the same for all ranks. The proportions of benzene, toluene, solvent naphtha, paraffins, and olefins in the light oils from the coals in any specific rank vary in a seemingly completely erratic manner. Within limits, the composition of coke-oven light oils, from the standpoint of refining procedures, is a function rather of the carbonization conditions than of the nature of the coal.

Finally, some of the properties of light oil depend upon the extent to which the gas is subjected to physical and chemical treatment before light-oil recovery. At coke ovens operated at gas plants, the send-out gas is highly purified to statutory limits of hydrogen sulfide, hydrogen cyanide, etc. The light-oil plant may well be the last step in the purification system, and in such circumstances the product will be free of hydrogen sulfide and readily adaptable to simple refining procedures. At steel mills, gas purification is often restricted to tar and ammonia removal; hence, the light-oil plant will treat gas containing most of the hydrogen sulfide and hydrogen cyanide present in the original raw oven gas.

It may be well at this point to define the nomenclature employed in this chapter. The ending -ene as in benzene, toluene, xylene, is used whenever reference to the

7 Schütz, F., and Buschmann, W., *Stahl u. Eisen*, **45**, 1232–42 (1925). *Dept. Sci. Ind. Research (Brit.), Fuel Research, Tech. Paper* **32** (1932), 123 pp. Bristow, W. A., *J. Inst. Petroleum Tech.*, **22**, 583–94 (1936).

8 Voss, W. A., *J. Soc. Chem. Ind.*, **46**, 373–5T (1927). **49**, 343–8T (1930). Hollings, H., Pexton, S., and Chaplin, R., *Trans. Inst. Chem. Engrs. (London)*, **7**, 85–107 (1929). Adam, W. G., and Anderson, G. W., *Gas World*, **105**, 28–31 (1936).

9 Fieldner, A. C., and Davis, J. D., *U. S. Bur. Mines, Monograph* **5** (1934), 164 pp.

10 *Proc. Am. Soc. Testing Materials, Pt. 1, Rept. Sect. Com.*, **34**, 463–80 (1934).

pure chemical entity is intended. The ending -ol, on the other hand, refers to marketable products prepared to the usual trade specifications. Thus, one can speak of 1° Benzol, 2° Benzol, Industrial Toluol, etc. (In English practice it is common to add a final e to the names of commercial distillates, giving Pure Benzole, Motor Benzole, 90's Benzole, Industrial Benzole, etc.) In addition, the -ol ending will be used in such phrases as "crude benzol," "crude toluol"; here the sense is simply that the cut is characterized by a high concentration of benzene or toluene. Finally, the -ol ending will be used in many places simply because of the restriction placed upon the -ene usage.

Not enough detailed data on American light oils are available to validate a presentation of any *average* analysis. The analysis given in Table II may be said to be that of a *typical* product. Gleaned from many sources, the data are a composite of analyses and do not represent a complete investigation of any given oil. The components are grouped in fractions or cuts that correspond to those obtained in a systematic separation of crude light oil by reasonably effective fractional distillation.

It is unfortunate that some of the valuable work done on the detailed composition of light oil is old and was restricted to studies of light oil obtained by the distillation of coal tar. Assuming equivalent boiling ranges, any compound found in coal-tar light oil can be demonstrated to be present in the light oil obtained from the corresponding coke-oven gas. As a result, data pertaining to the existence of compounds in light oil from coal tar have been often extrapolated to coke-oven light oils in general.

FORERUNNINGS

Ordinarily, this most volatile fraction will constitute from 1 to 3 percent by volume

TABLE II

ANALYSIS OF A TYPICAL CRUDE COKE-OVEN LIGHT OIL

	Percentages by Volume
I. Forerunnings.	
Cyclopentadiene	0.5
Carbon disulfide	0.5
Amylenes and unidentified	1.0
II. Crude benzol.	
Benzene	57.0
Thiophene	0.2
Saturated nonaromatic hydrocarbons, unidentified	0.2
Unsaturates, unidentified	3.0
III. Crude toluol.	
Toluene	13.0
Saturated nonaromatic hydrocarbons, unidentified	0.1
Unsaturates, unidentified	1.0
IV. Crude light solvent.	
Xylenes	5.0
Ethyl benzene	0.4
Styrene	0.8
Saturated nonaromatic hydrocarbons	0.3
Unsaturates, unidentified	1.0
V. Crude heavy solvent.	
Coumarone, indene, dicyclopentadiene	5.0
Polyalkyl benzenes, hydrindene, etc.	4.0
Naphthalene	1.0
Unidentified "heavy oils"	1.0
VI. Wash oil	5.0 *
Total	100.0

* The amount of wash oil present depends greatly upon the performance and design of the debenzolization apparatus as well as upon the nature of the wash oil employed.

of the crude light oil. Its precise composition is susceptible to slight changes in plant operations and may vary from day to day in a quite unaccountable manner. Highly

unsaturated, its chief components are found to be cyclopentadiene (C_5H_6, b.p. 41–2° C), carbon disulfide (CS_2, b.p. 46.25° C), and the amylenes (C_5H_{10}, b.p. 20.1 to 38.6° C). Butadiene-1,3 [11] (C_4H_6, b.p. −4.5° C) and butene-1 [12] (C_4H_8, b.p. −6.47° C) have also been reported. Hydrogen sulfide (H_2S, b.p. −59.6° C), hydrogen cyanide (HCN, b.p. 26° C), carbonyl sulfide (COS, b.p. −50.2° C), methyl mercaptan (CH_3-SH, b.p. 7.6° C), ethyl mercaptan (C_2H_5-SH, b.p. 34.7° C), and dimethyl sulfide ((CH_3)$_2$S, b.p. 36.2° C) are all found, the last three, being thermally unstable,[13] in barely detectable amounts. N-pentane, hexene-1, butyne-2, and acetone have been found in high-temperature coal-tar light oil [14] and are presumably also present in the light oil in gas.

Cyclopentadiene, HC————CH, is of

$$HC \quad\quad CH$$
$$\backslash \quad /$$
$$CH_2$$
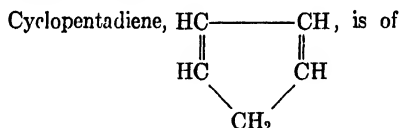
particular interest since its recovery from the forerunnings fraction is practiced on a commercial scale. As would be expected from the conjugated double bond structure, this substance is highly unstable and reactive. Polymerization to the dimer dicyclopentadiene ($C_{10}H_{12}$, m.p. 32.9° C, b.p. 170° C) proceeds rapidly at ordinary temperatures in the liquid and gaseous phase and in a forerunnings solution. The dimer is relatively stable on storage and can be decomposed almost quantitatively to the monomer by distillation at atmospheric pressure. On a commercial scale, recovery of cyclopentadiene is based on thermal polymerization to the dimer and subsequent separation of the high-boiling dicyclopentadiene from the unpolymerized residual forerunnings. Superatmospheric pressures may be employed.[15] With aldehydes and ketones, in the presence of alkaline condensing agents, cyclopentadiene gives a series of brightly colored compounds,[16] the fulvenes, which have been thought to be responsible for the color of light oils. In the laboratory fractionation of crude light oils the writer has noticed that, although crude benzols are usually very light in color, a sudden increase in deepness of the yellow hue of the distillate is noticed when the vapor temperature reaches 110° (or the toluol plateau). As the distillation of crude toluol progresses, this color fades but deepens again when the xylol plateau is reached. There seems to be no definite information concerning the identity of the colored compounds.

The Diels-Alder [17] condensation with maleic anhydride provides a convenient method for the analytical determination of the cyclopentadiene.[18] If crude light oils are washed with sulfuric acid without previous removal of the forerunnings, the thermal treatment in the pure still distillation may often result in a "corrosive" product. Claxton and Hoffert [19] found that the amount of sulfur dioxide produced was roughly proportional to the cyclopentadiene and dicyclopentadiene content. The in-

11 Lunge, G., *Coal-Tar and Ammonia*, Van Nostrand Company, New York, 5th ed., 1916, p. 219.

12 Ahrens, F. B., *Z. angew. Chem.*, **17**, 1518 (1904).

13 Faragher, W. F., Morrell, J. C., and Comay, S., *Ind. Eng. Chem.*, **20**, 527–32 (1928).

14 Fisher, C. H., *U. S. Bur. Mines, Bull. 412* (1938), 70 pp.

15 Ward, A. L., U. S. Pat. 2,211,038 (1940).

16 Thiele, J., *Ber.*, **33**, 666–73 (1900).

17 Diels, O., and Alder, K., *Ann.*, **460**, 98–122 (1928).

18 Grosse, A. V., Morrell, J. C., and Mavity, J. M., *Ind. Eng. Chem.*, **32**, 309–11 (1940). Kirsanov, A. V., Polyakova, I. M., and Kuznetsova, Z. I., *J. Applied Chem. (U.S.S.R.)*, **13**, 1406–13 (1940).

19 Claxton, G., and Hoffert, W. H., *Gas World*, **113**, No. 2927, Coking Sect., 70–6 (1940).

clusion of the continuous forerunnings stripping column in the light-oil-recovery plant provides a fundamental solution to the problem of corrosive products. At such an installation Preston and van der Hoeven [20] found that usually a caustic vapor neutralizer on the pure still was unnecessary.

Polymerization of dicyclopentadiene at 260° C to form useful resins has been carried out on a commercial scale.[21] The product is of low molecular weight, heat stable, color stable below 225° C, resistant to acids, alkalies, brines, alcohol, glycol, glycerol, etc., and is odorless, tasteless, and nontoxic.

Cyclopentadiene is an attractive raw material to organic and physical chemists and is consequently endowed with a voluminous literature. In addition to the traditional studies of derivatives [22] much attention has been directed to examinations of the mechanism of the polymerization and depolymerization reactions.[23]

[20] Preston, E., and van der Hoeven, B. J C., *Blast Furnace Steel Plant*, **28**, 455–60 (1940).

[21] Carmody, W. H., Sheehan, W., and Kelly, H., *Ind. Eng. Chem.*, **30**, 245–51 (1938).

[22] Brooks, B. T., *Chemistry of Non-Benzenoid Hydrocarbons*, Chemical Catalog Co., New York, 1922, 612 pp. Wieland, H., Bergel, F., Schwartz, K., Schepp, R., and Fukelman, I., *Ann.*, **446**, 13–31 (1926). Staudinger, H., and Bruson, H. A., *ibid.*, **447**, 97–110 (1926). Horclois, B., *Chimie & industrie*, Spec. No., 357–63, April, 1934. Alder, K., and Holzrichter, H., *Ann.*, **524**, 145–80 (1936). Ellis, C., *The Chemistry of Petroleum Derivatives*, II, Reinhold Publishing Corp., New York, 1937, 1464 pp.

[23] Stobbe, H., and Reuss, F., *Ann.*, **391**, 151–68 (1912). Barrett, E. G. V., and Burrage, L. J., *J. Phys. Chem.*, **37**, 1029–35 (1933). Alder, K., and Stein, G., *Angew. Chem.*, **47**, 837–42 (1934). Schultze, G. R., *J. Am. Chem. Soc.*, **56**, 1552–6 (1934); *Oel, Kohle, Erdoel, Teer*, **14**, 113–7 (1938). Khambata, B. S., and Wasserman, A., *Nature*, **137**, 496–7 (1936), **138**, 368–9 (1936). Kistiakowsky, G. B., and Mears, W. H., *J. Am. Chem. Soc.*, **58**, 1060 (1936). Raistrick, B., Sapiro, R. H., and Newitt, D. M., *J. Chem. Soc.*, **1939**, 1761–9

CRUDE BENZOL

Usually, from 55 to 70 percent by volume of the crude light oil will be represented by the benzol fraction. In addition to the major compound (C_6H_6; b.p. 80.09° C), the crude cut contains from 3 to 7 percent of unsaturated hydrocarbons (chiefly monoolefins), perhaps as much as 2 percent of saturated hydrocarbons, and from 0.2 to 0.5 percent of the most troublesome impurity, thiophene. Information on the hydrocarbon impurities is very scanty; their specific identity is almost completely unknown. Kruber [24] adduced evidence suggesting the probable presence of hexenes, heptenes, and cyclohexenes. The diolefins, existing in relatively small proportions, are believed to be chiefly responsible for the instability and gum-forming tendencies of only partially refined motor benzols. The high octane rating of the monoolefins has led to the invention of motor-fuel refining techniques directed either to the selective removal of the diolefins or the inhibition of their reactivity by the addition of small quantities of phenolic compounds.

Diethyl sulfide, methyl ethyl ketone, acetonitrile, cyclohexadiene, *n*-hexane, *n*-heptane, and cyclohexane probably exist in small amounts since all have been isolated from high-temperature coal tar.[14] The removal of cyclohexane (C_6H_{12}, b.p. 80.7° C) by means of azeotropic distillation with acetone has been proposed.[25]

Although traces of other sulfur compounds may be present it is usually assumed that the sulfur content of this crude benzol fraction is entirely represented by thiophene (C_4H_4S, b.p. 85° C). Thiophene is a high-temperature pyrolysis product [18] and is not found in low-temperature light

[24] Kruber, O., *Brennstoff-Chem.*, **13**, 187–90 (1932).

[25] Field, E., U. S. Pat. 2,212,810 (1940).

oils. The mode of formation of thiophene in the carbonization process is completely conjectural.

On a commercial scale thiophene-free benzol may be prepared from commercially pure benzols by drastic washing with sulfuric acid. Originally devised by Victor Meyer in 1883, the process depends upon the observation that, under carefully controlled conditions, substantial sulfonation of thiophene will take place with only slight destruction of benzene. Small amounts of fuming acid are effective at relatively low temperatures. In the preparation of low-sulfur motor fuels from very high sulfur-bearing crudes, some acid washing, with the concomitant unavoidable destruction of unsaturates, may be necessary. In such circumstances Hoffert, Claxton, and Hancock [26] found that, for any particular oil and for any given removal of thiophene, the refining losses were constant and independent of the strength and quantity of acid used to effect this removal. Another important conclusion was that even with amounts of acid up to 7 percent by volume it was impossible to reduce the thiophene-sulfur content of a benzol to a low figure without using fairly strong acid.[6] The nature of the unsaturates present seems to have considerable effect on the efficiency of thiophene removal. Styrene and indene are particularly effective and, if a washed solvent is being manufactured, may well be included with the benzol during washing, the separation by fractional distillation being carried out on the washed material. Kruber [24] believed that the mechanism of thiophene removal by sulfuric acid could be explained through the formation of condensation products with the unsaturates. The deliberate admixture of cyclopentadiene before acid washing has been

proposed.[27] Since the time of Victor Meyer, who himself suggested treatment with bromine followed by a caustic wash, numerous processes have been devised utilizing agents other than sulfuric acid. The reader will find some of these discussed in a later section of this chapter (see page 1198).

CRUDE TOLUOL

Comprising 12 to 20 percent by volume of the light oil, this fraction will include, in addition to the main aromatic hydrocarbon toluene, from 5 to 10 percent by volume (in terms of the fraction) of unsaturated hydrocarbons, 0.1 to 4.0 percent by volume of paraffins plus naphthenes, and small quantities of the methyl thiophenes. Information about the specific identity of the "paraffins" and unsaturates is more or less speculative. N-heptane, n-octane, methyl cyclohexane, dimethyl cyclohexane, and pyridine are found in the corresponding fraction of coal-tar light oil.

The specific-gravity specification of nitration toluol does not tolerate the presence of much more than 1.5 percent of paraffin or naphthenic hydrocarbons. The impurities are characterized chemically by an indifference to most reagents and physically by boiling properties sufficiently close to those of toluene to make conventional fractional distillation quite ineffective as a purification procedure. Practically all the paraffins occurring in the crude toluol fraction will find their way into the refined product. Usually the trouble can be avoided by a proper adjustment to coke-oven operation since the paraffin content of toluols is closely related to oven heats and coking times. Under normal business conditions, when ovens are generally pushed on a fast schedule, little difficulty is experienced.

26 Hoffert, W. H., Claxton, G., and Hancock, E. G., *Gas J.*, **214**, 103–5, 167–71 (1936).

27 Kopelevich, G. V., Brodovich, A. I., and Hecht, I. R., *Coke and Chem.* (*U.S.S.R.*), **1935**, No. 7, 19–22.

Unacceptable amounts of paraffins are usually associated with the low oven temperatures and long coking times appropriate to depressed economic conditions. A few operators have found a solution in the practice of pushing some oven blocks empty while the remaining batteries are operated at normal speeds.[28] Azeotropic distillation has been utilized in the laboratory to effect the separation of paraffins and toluene. Good results have been attained by the use of methyl cyanide as the azeotropising agent.[29]

CRUDE LIGHT SOLVENT

This relatively small fraction, 4 to 8 percent of the original crude, will consist, in the main, of the three xylenes $(C_6H_4(CH_3)_2$, o, m, and p; b.p. 144.50° C, 139.10° C, 138.44° C), ethyl benzene $(C_6H_5C_2H_5$, b.p. 136.15° C), styrene $(C_6H_5CH=CH_2$, b.p. 145.2° C), and small quantities of dimethyl thiophenes, unidentified unsaturated and saturated nonaromatic hydrocarbons. The yield of aromatics will be from 65 to 75 percent, and total "unsaturates" (including styrene) will range from 20 to 25 percent.

Most authorities agree in believing commercial xylol, or light solvent naphtha, to be chiefly metaxylene. Kishner and Krasova [30] have reported as follows for the refined product: m-xylene, 68 to 70; p-xylene, 18 to 19; o-xylene, 3 to 5; and ethyl benzene, 7 to 9 percent, respectively.

The attractive possibility of extracting the pure isomers from the commercial mixture awaits the invention of a suitable process. Some separation can be obtained by selective oxidation [31] or sulfonation,[32] by fractional crystallization of the sodium or calcium sulfonates,[33] and by such physical means as direct crystallization [34] of the isomers.

Styrene is present in crude coke-oven light oils in amounts ranging up to 1 percent (average 0.8 percent). Used as a raw material in the manufacture of emulsifying agents, synthetic resins,[35] and buna rubbers, most of the material now sold is a synthetic product. The recovery of natural styrene is not practiced on a large commercial scale.

The saturated aliphatic and naphthenic hydrocarbons are present in this fraction in somewhat higher concentration than the corresponding compounds in coke-oven benzol and toluol. Virtually nothing is known about these constituents; in general their boiling points lie somewhat higher than the boiling point of an average mixture of the isomeric xylenes.

Possible constituents, because of their reported isolation from coal tar, are: isopropyl benzene, pyrrole, methyl pyridine, and dimethyl pyridines.

CRUDE HEAVY SOLVENT AND WASH OIL

The "crude heavy solvent," varying from a few percent to 10 percent of the light oil, is characterized by great complexity and the profound dependence of its composition upon both the design of the crude stripping

[28] Denig, F., *Iron Steel Engr.*, **15**, No. 10, 32–53, 63 (1938).

[29] Rossini, F. D., Mair, B. J., and Glasgow, A. R., Jr., *J. Research Natl. Bur. Standards*, **27**, 39–63 (1941); *Oil Gas J.*, **39**, No. 27, 158–9, 219 (1940).

[30] Kishner, N., and Krasova, V., *J. Gen. Chem.* (*U.S.S.R.*), **6**, 748–56 (1936).

[31] Reuter, A., *Ber.*, **17**, 2028–9 (1884). Clarke, H. T., and Taylor, E. R., *J. Am. Chem. Soc.*, **45**, 830–3 (1923).

[32] Jacobsen, O., *Ber.*, **10**, 1010–5 (1877). Friedel, M., and Crafts, J. M., *Compt. rend.*, **114**, 1110–3 (1892). Lepers, P., U. S. Pat. 1,311,848 (1919).

[33] Patterson, T. S., McMillan, A., and Somerville, R., *J. Chem. Soc.*, **1924**, 2488–90.

[34] Spannagel, H., and Tschunkur, E., U. S. Pat. 1,940,065 (1933).

[35] Ellis, C., *The Chemistry of Synthetic Resins*, Reinhold Publishing Corp., New York, 1935, pp. 232–62.

and rectification apparatus and the efficiency of debenzolization of the absorbent oil. Preeminently a function of the details of the recovery plant, it may be approximately defined for any one installation as the residuum of crude benzol, toluol, and xylol separation from unrefined light oil.

Among the unsaturated components will be found dicyclopentadiene ($C_{10}H_{12}$, b.p. 170° C) and commercially significant quantities of coumarone (C_8H_6O, b.p. 175° C) and indene (C_9H_8, b.p. 182.0° C). The last two find important use in the preparation of a wide variety of paracoumarone-indene resins. Dicyclopentadiene usually appears only in solvent prepared from crude light oil that has been stored for some time.

The aromatic hydrocarbons are represented by a mixture of mono- and polyalkyl benzenes, naphthalene, and hydronaphthalenes. The various trimethyl benzenes are found in significant amounts.

All the absorbent oil originally contaminating the crude light oil will be concentrated in this fraction. In some modes of operation, and particularly in older installations, wash oil will make up the bulk of "crude heavy solvent." In America where a petroleum wash oil is exclusively used the contaminants will be paraffinic and naphthenic in nature. In Great Britain, where creosote wash oils are extensively employed, the heavy solvent may contain large quantities of the lower-boiling hydroxybenzenes. In German practice the converse is true since the removal of tar acids and naphthalene from all tars is mandatory by governmental edict and German creosote wash oils are hence relatively free of these materials. Probably present in traces will be the very large number of compounds of appropriate boiling point that have been found in high-temperature coal tar. These are included in Table III, a summary of some of the physical properties of the individual components in light oil. Table III presents only compounds that have been found in high-temperature coke-oven light oil or in the light-oil fraction of coal tar.

TABLE III

PHYSICAL PROPERTIES OF THE CONSTITUENTS OF LIGHT OIL *

		Boiling Point	Melting Point	Density $d_{4°}^{20°}$ unless Otherwise Noted	Refractive Index $n_D^{20°}$ unless Otherwise Noted
		°C at 760 mm	°C		
Aromatic hydrocarbons					
benzene	C_6H_6	80.09	5.53	0.8737(25°)	1.4981(25°)
toluene	$C_6H_5CH_3$	110.61	−95.0	0.8670	1.4969
o-xylene	$C_6H_4(CH_3)_2$	144.50	−25.2	0.8801	1.5071
m-xylene	$C_6H_4(CH_3)_2$	139.10	−47.9	0.866	1.4970
p-xylene	$C_6H_4(CH_3)_2$	138.44	13.3	0.8610	1.4986
ethyl benzene	$C_6H_5C_2H_5$	136.15	−94.4	0.8667	1.4985(15°)
hydrindene	$C_6H_4CH_2CH_2CH_2$	178.0	−51	0.9639	1.5383
isopropyl benzene	$C_6H_5CH(CH_3)_2$	152.4	−96.2	0.8581	1.4912
o-ethyl toluene	$CH_3C_6H_4C_2H_5$	164.9	−88	0.881	1.5042
m-ethyl toluene	$CH_3C_6H_4C_2H_5$	161.5		0.869(17°)	1.4975
p-ethyl toluene	$CH_3C_6H_4C_2H_5$	161.2	−64	0.866	1.4832
n-propyl benzene	$C_6H_5CH_2CH_2CH_3$	158.6	−89.2	0.8628	1.4919
mesitylene	$C_6H_3(CH_3)_3$	164.6	−44.7	0.8653	1.4967(25°)
pseudocumene	$C_6H_3(CH_3)_3$	169.2	−44.1	0.8762	1.5025(25°)

TABLE III—*Continued*

PHYSICAL PROPERTIES OF THE CONSTITUENTS OF LIGHT OIL *

		Boiling Point	Melting Point	Density $d_{4°}^{20°}$ unless Otherwise Noted	Refractive Index $n_D^{20°}$ unless Otherwise Noted
		°C at 760 mm	°C		
Aromatic hydrocarbons					
hemimellitene	$C_6H_3(CH_3)_3$	176.2	−25.4	0.8944	1.5130
naphthalene	$C_{10}H_8$	217.6	80.3	1.145	1.5823(98.4°)
(1,2-dihydronaphthalene) †	$C_{10}H_{10}$		−9	0.997	
(1,4-dihydronaphthalene) †	$C_{10}H_{10}$	212	25	0.998	1.5740(14.7°)
tetrahydronaphthalene	$C_{10}H_{12}$	206.8	−30.0	0.9707	1.5438
(o-cymene) †	$CH_3C_6H_4CH(CH_3)_2$	175.5	−73.5	0.876	1.5003
(m-cymene) †	$CH_3C_6H_4CH(CH_3)_2$	175.7	−75.0	0.8606	1.4920
(p-cymene) †	$CH_3C_6H_4CH(CH_3)_2$	177.3	−68.8	0.8570	1.4904
durene	$C_6H_2(CH_3)_4$	196.0	79.3	0.8380(81.3°)	1.463(90°)
isodurene	$C_6H_2(CH_3)_4$	198.0	−24.0	0.8906	1.5134
Paraffin hydrocarbons					
n-pentane	C_5H_{12}	36.08	−129.7	0.62638	1.35768
n-hexane	C_6H_{14}	68.8	−94.0	0.65942	1.37506
n-heptane	C_7H_{16}	98.4	−90.5	0.68375	1.38774
n-octane	C_8H_{18}	125.6	−56.8	0.70283	1.39764
n-decane	$C_{10}H_{22}$	174.04	−29.72	0.72985	1.41205
Saturated cyclic hydrocarbons					
cyclohexane	C_6H_{12}	80.8	6.5	0.7782	1.4265
methylcyclohexane	$C_6H_{11}CH_3$	100.3	−126	0.7693	1.4231
(1,1-dimethylcyclohexane) †	$C_6H_{10}(CH_3)_2$	120	−34	0.7810	1.4293
(1,2-dimethylcyclohexane) †	$C_6H_{10}(CH_3)_2$	126		0.79	1.43
(1,3-dimethylcyclohexane) †	$C_6H_{10}(CH_3)_2$	121		0.77	1.42
(1,4-dimethylcyclohexane) †	$C_6H_{10}(CH_3)_2$	121		0.77	1.42
Olefin hydrocarbons					
1-butene	C_4H_8	−6.47	< −195	0.6255(−6.47°)	1.3803(−25°)
1-pentene	C_5H_{10}	30.1		0.6429	1.3714
1-hexene	C_6H_{12}	63.5	−138	0.6747	1.3886
cyclohexene	C_6H_{10}	83	−80	0.8098	1.4465
1-heptene	C_7H_{14}	93.1	−119.1	0.6976	1.3999
Diolefin hydrocarbons					
1,3-butadiene	$CH_2:CHCH:CH_2$	−4.5	−108.7	0.650(−6°)	1.422(−6°)
2-butyne ‡	$CH_3C:CCH_3$	28		0.6937	1.3939
cyclopentadiene-1,3	$CH:CHCH:CHCH_2$	41–2	−85	0.805	1.44
(cyclohexadiene) ‡	C_6H_8	82–3		0.846	1.47(21.2°)
(cyclohexadiene 1,3) ‡	C_6H_8	81–2	−98	0.84	1.47
(cyclohexadiene 1,4) ‡	C_6H_8	84–7		0.85	1.47
dicyclopentadiene	$C_{10}H_{12}$	170	32.9	0.9756(35°)	
Aromatic hydrocarbons with unsaturated side chains					
styrene	$C_6H_5CH:CH_2$	145.2	−31	0.9038(23°)	1.5440(23°)
indene	$C_6H_4CH_2CH:CH$	182.0	−1.5	0.9968	1.5768
(2-methyl indene) †	$C_{10}H_{10}$	185–6		0.9897(14°)	1.5757(14°)
(3-methyl indene) †	$C_{10}H_{10}$	198.5		0.9640	1.5591(27°)
Neutral oxygen compounds					
acetone	CH_3COCH_3	56.24	−94.3	0.7898	1.359
methylethyl ketone	$CH_3COC_2H_5$	79.60	−86.4	0.8101	1.379

TABLE III—*Continued*
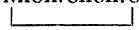
PHYSICAL PROPERTIES OF THE CONSTITUENTS OF LIGHT OIL *

		Boiling Point	Melting Point	Density $d_4^{20°}$ unless Otherwise Noted	Refractive Index $n_D^{20°}$ unless Otherwise Noted
		°C at 760 mm	°C		
Neutral oxygen compounds					
coumarone	$C_6H_4OCH:CH$	175	<-18	1.091	
acetophenone †	$C_6H_5COCH_3$	201.0	19.65	1.0238(25°)	1.5342(19.6°)
(2-methyl coumarone) †	C_9H_8O	198		1.054	1.5614
(3-methyl coumarone) †	C_9H_8O	198		1.054(23.4°)	1.553(23.1°)
(5-methyl coumarone) †	C_9H_8O			1.0603(19.2°)	1.557(19°)
(6-methyl coumarone) †	C_9H_8O	192–3			
(7-methyl coumarone) †	C_9H_8O	190–1		1.049(19°)	1.5525(17°)
Neutral and acidic nitrogen compounds					
hydrogen cyanide	HCN	26	−14	0.669	1.267(10°)
acetonitrile	CH_3CN	82	−41	0.7828	1.3474
benzonitrile	C_6H_5CN	190.7	−13	1.008(16.8°)	1.5289
Phenols					
phenol	C_6H_5OH	182	41	1.071(25°)	1.542(41°)
o-cresol	$CH_3C_6H_4OH$	190.8	30.1	1.0465	1.5453
m-cresol	$CH_3C_6H_4OH$	202.8	10	1.0336	1.5398
p-cresol	$CH_3C_6H_4OH$	202.3	34.8	1.0341	1.5395
2,3-dimethyl phenol	$(CH_3)_2C_6H_3OH$	218	75		
2,4-dimethyl phenol	$(CH_3)_2C_6H_3OH$	211.5	27–8	1.0276(14°)	1.5420(14°)
2,5-dimethyl phenol	$(CH_3)_2C_6H_3OH$	211.5	75		
2,6-dimethyl phenol	$(CH_3)_2C_6H_3OH$	212	49		
3,4-dimethyl phenol	$(CH_3)_2C_6H_3OH$	225.1	65		
3,5-dimethyl phenol	$(CH_3)_2C_6H_3OH$	219.5	68		
o-ethyl phenol	$C_2H_5C_6H_4OH$	207.5	•	1.037(0°)	
m-ethyl phenol	$C_2H_5C_6H_4OH$	214	−4	1.025(0°)	
p-ethyl phenol	$C_2H_5C_6H_4OH$	219	47		
Basic nitrogen compounds			•		
pyrrole	NHCH:CHCH:CH	131		0.948	1.5085
pyridine	C_5H_5N	115.3	−42	0.982	1.509
aniline	$C_6H_5NH_2$	184.4	−6.2	1.0214	1.5868
2-methyl pyridine	$CH_3C_5H_4N$	129	−69.9	0.950	1.5029(17°)
3-methyl pyridine	$CH_3C_5H_4N$	143.5	−17.9	0.952	1.5043(24°)
4-methyl pyridine	$CH_3C_5H_4N$	143.1	+3.5	0.957	1.5064(19°)
o-toluidine	$CH_3C_6H_4NH_2$	200.8	−16.25	1.004	1.5688
2,3-dimethyl pyridine	$(CH_3)_2C_5H_3N$	163.4			
2,4-dimethyl pyridine	$(CH_3)_2C_5H_3N$	157		0.938(14°)	1.503
2,5-dimethyl pyridine	$(CH_3)_2C_5H_3N$	159			
2,6-dimethyl pyridine	$(CH_3)_2C_5H_3N$	142.5	−6.0	0.932(25°)	
3,4-dimethyl pyridine	$(CH_3)_2C_5H_3N$	164.5	•		
(3,5-dimethyl pyridine) †	$(CH_3)_2C_5H_3N$	170.1			
dimethyl aniline	$C_6H_5N(CH_3)_2$	192	2.1	0.9557	1.5582
2,4,5-trimethyl pyridine	$(CH_3)_3C_5H_2N$	168		0.966	
2,4,6-trimethyl pyridine	$(CH_3)_3C_5H_2N$	172		0.917(15°)	
(2,3,4-trimethyl pyridine) †	$(CH_3)_3C_5H_2N$	192–3		0.9127(15°)	
(2,3,5-trimethyl pyridine) †	$(CH_3)_3C_5H_2N$	183–4			
(2,3,6-trimethyl pyridine) †	$(CH_3)_3C_5H_2N$	176–8			

TABLE III—*Continued*

PHYSICAL PROPERTIES OF THE CONSTITUENTS OF LIGHT OIL *

Sulfur compounds		Boiling Point	Melting Point	Density $d_4^{20°}$ unless Otherwise Noted	Refractive Index $n_D^{20°}$ unless Otherwise Noted
		°C at 760 mm	°C		
sulfur	S	444.6	114–120		
hydrogen sulfide	H_2S	−59.6	−82.9	0.96(−60°)	
carbonyl sulfide	COS	−50.2	−138	1.24(−87°)	
carbon disulfide	CS_2	46.25	−111.6	1.2661	1.6319(15°)
methyl mercaptan	CH_3SH	7.6	−123	0.868	
ethyl mercaptan	C_2H_5SH	34.7	−147.3	0.840	1.430
dimethyl sulfide	$CH_3)_2S$	36.2	−83.2	0.849	
diethyl sulfide	$C_2H_5)_2S$	91.6	−102.1	0.837	1.442
thiophene	C_4H_4S	85	−40	1.065	1.528
2-methyl thiophene	$CH_3C_4H_3S$	112	−51	1.016	
3-methyl thiophene	$CH_3C_4H_3S$	115		1.025	
(2,3-dimethyl thiophene) †	$CH_3)_2C_4H_2S$	140–1		0.994	
(2,4-dimethyl thiophene) †	$CH_3)_2C_4H_2S$	138		0.9956	
(2,5-dimethyl thiophene) †	$CH_3)_2C_4H_2S$	137.5		0.9859(19°)	1.5142
(3,4-dimethyl thiophene) †	$CH_3)_2C_4H_2S$	146		$1.008\binom{23°}{22°}$	
(2,3,4-trimethyl thiophene) †	$CH_3)_3C_4HS$	162			
thionaphthene	$C_6H_4SCH:CH$	221	32	1.165	1.6332(36°)

* A partial list of the sources used in compiling this table is as follows: *International Critical Tables*, McGraw Hill Book Co., New York, 1926–33. Heilbron, I. M., et al., *Dictionary of Organic Compounds*, Oxford University Press, New York, 1934–9. Hoffert, W. H., and Claxton, G., ref. 6. Doss, M. P., *Physical Constants of the Principal Hydrocarbons*, The Texas Company, New York, 1939, 152 pp. Egloff, G., *Physical Constants of Hydrocarbons*, Vols. I, II, Reinhold Publishing Corp., New York, 1939–40, 403 and 605 pp.

† The use of parentheses indicates that the compound has been identified only as a mixture of isomers.

‡ Acetylene derivative.

THE COMMERCIAL DISTILLATES OBTAINED FROM LIGHT OIL

From the viewpoint of practical utilization, most of the hundred-odd constituents of light oil can be considered impurities. Economically, the composition of light oil is best referred, not to the many individual chemical species, but to the relatively few distillates commercially produced. On the basis of rather broad and inclusive census classifications, as shown in Table I, the commercial derivatives of American light oil are as shown in Table IV.

In individual works, production figures provide a convenient practical analysis of the crude light oil. The nature of the coal gas, the technological age of the recovery and refining plant, and the current market for particular distillates are all reflected in the wide variation in reported data. Preston and van der Hoeven [20] have presented interesting information for a 1939 installation. Of the semi-continuous type, the plant included a continuous forerunnings stripper, a continuous motor-fuel distillation column, and a large batch still, the last being used in the preparation of pure benzol, toluol, xylol, etc. The detailed performance of such a purification scheme gave the following derived analysis for the

TABLE IV

COMMERCIAL DERIVATIVES OF AMERICAN LIGHT OIL IN PERCENTAGES OF THE TOTAL

	1935	1936	1937	1938	1939	1940
Benzol, crude and refined	15.1	11.4	11.6	14.4	14.8	14.8
Motor benzol	43.7	50.3	51.1	45.6	46.6	47.0
Toluol, crude and refined	12.0	11.6	11.2	10.5	11.6	12.3
Solvent naphtha	3.0	3.0	3.1	3.0	2.8	2.4
Xylol	2.8	2.5	2.4	2.3	2.4	2.6
Other light-oil products	3.9	3.9	4.3	4.4	3.7	3.5
Total derived products	80.4	82.8	83.7	80.3	81.8	82.6
Refining losses, used on premises, etc.	19.6	17.2	16.3	19.7	19.2	17.4
Total	100.0	100.0	100.0	100.0	100.0	100.0

light oil as percentages of the total crude feed:

Motor fuel	22.83
1° Benzol	44.50
2° Benzol	0.67
1° Toluol	12.01
2° Toluol	3.03
Pure xylol	4.31
Washed heavy solvent	0.64
Crude heavy solvent	1.12
Total salable products	89.11
Residue	5.32
Washing loss	3.62
Loss from forerunnings vaporized into fuel gas, distillation, handling, etc.	1.95

The commercial distillates obtained from coke-oven crude light oil refined on the premises are relatively few in number. Depending upon the flexibility of the plant, the light-oil producer, through variation of the intensiveness of refining and by blending, can supply special fractions or blends to almost any specification. In general, however, production is to relatively well-established consumer specifications and is principally restricted to about fifteen standard distillates. Some of the properties of these materials, as assembled from average current specifications, are summarized in Table V. The development of new syntheses placing emphasis on the absence of impurities formerly considered tolerable

and the competitive market conditions can be expected to lead to increasingly rigid manufacturing specifications. In growing number, new important uses will be developed in addition to those outlined briefly below.

Thiophene-Free Benzol. A small amount of this material is prepared for use as an analytical reagent and as a raw material in the preparation of fine chemicals. Thiophene is an active catalyst poison, forms resins in aluminum chloride condensations, contributes to the instability of aniline, and interferes markedly in the preparation of resorcinol and similar compounds.

1° Nitration Benzol. As its name implies, this distillate is used in the preparation of nitrobenzols when especial purity is required. As a raw material, it finds application in the manufacture of aniline, chlorobenzene, cyclohexane, diphenylamine, phenol, styrene, dye intermediates, etc. Its use as a solvent is restricted to special purposes where great purity is required.

Industrial Pure Benzol and 90 Percent Benzol. Two-degree benzol (Industrial Pure Benzol) is sufficiently pure to be used in large quantities as a chemical raw material and as a solvent; 90 percent benzol (about 85 percent benzene, 12 percent toluene, 3 percent xylene) sells at nearly the

TABLE V
PROPERTIES OF COMMERCIAL LIGHT-OIL DISTILLATES

Name	Distillation				Color [a]	Specific Gravity at 15.5° C	Acid Wash Test [b] Not darker than	Sulfur Compounds [a]	Copper Corrosion [a]
	First Drop °C	Percent at Fixed Temperature	Dry Point °C	Range °C					
Thiophene-free benzol [c,d]	≧79.2	All within 1° including 80.2° C	≦81.2	1	Water white	0.882-0.886	2	No H₂S, SO₂, CS₂ or C₄H₄S	None
Nitration benzol [c,d]	≧79.2	All within 1° including 80.2° C	≦81.2	1	Water white	0.882-0.886	2	No H₂S, no SO₂	None
Industrial pure benzol [c,d]	≧78.2	All within 2° including 80.2° C	≦82.2	2	Water white	0.875-0.886	3	No H₂S, no SO₂	None
Industrial 90% benzol [c,d]	≧78.2	At least 90% at 100° C	≦120	41.8	Water white	0.875-0.886	6	No H₂S, no SO₂	None
Motor benzol [c,d]	76-82	At least 60% at 100° C; at least 90% at 120° C	≦170	88-94	Water white	0.885-0.885	12	Total S ≦ 0.40%	Iridescent or peacock
Inhibited motor benzol [e,f]	70-82	At least 60% at 100° C; at least 90% at 120° C	≦170	88-100	0.0165 gm/l K₂Cr₂O₇	≧0.870	No test	Total S ≦ 0.40%	Iridescent or peacock
Nitration toluol [c,d]	≧109.4	All within 2° including 110.4° C	≦111.4	1	Water white	0.8690-0.8730	2	No H₂S, no SO₂	None
Industrial pure toluol [c,d]	≧108.4	All within 1° including 110.4° C	≦112.4	2	Water white	0.864-0.874	4	No H₂S, no SO₂	None
Nitration xylol [c,d]	≧137.2	All within 3° C	≦140.5	3	Water white	0.865-0.870	6	No H₂S, no SO₂	None
5° xylol [c,d]	≧137	All within 8° C	≦143	5	Water white	0.860-0.870	6	No H₂S, no SO₂	None
10° xylol [c,d]	≦135	All within 10° C	≦145	10	Water white	0.860-0.870	6	No H₂S, no SO₂	None
Industrial xylol [c,d,h,i]	≦135	Not over 5% at 130° C; 90 to 95% at 145° C	≦155	25-30	Water white	0.850-0.870	10	No H₂S, no SO₂	None
Refined heavy solvent [j]	≧150	90% at approx. 180° C	<185-200	35-50	Water white	0.855-0.890	9	No H₂S, no SO₂	Not specified
Crude light solvent [c,d]	≦135	Not over 5% at 130° C; 90-95% at 180° C	≦180	70-75	Dark straw	0.860-0.885	Not specified	Not specified	Not specified
Crude heavy solvent [c,d,k]	Not over 5% at 165°	5% at 150° C; at least 90% at 200° C	≦220		Deep amber to dark red	0.885-0.988	Not specified	Not specified	Not specified

[a] A.S.T.M., D 268-33.
[b] Gas Chemists' Handbook, Am. Gas Assoc., New York, 1929, p. 389.
[c] No acidity.
[d] No foreign odor.
[e] Solidifying point not below plus 4.85° C.
[f] Inhibited with a substituted para-aminophenol type gum inhibitor, and not to contain more than 5 mg per 100 ml of preformed gum nor more than 20 mg per 100 ml of oxidation gum.
[g] Paraffin content shall not exceed 4 percent.
[h] Paraffin content not over 10 percent.
[i] Almost identical with "refined solvent naphtha."
[j] Available in various grades.
[k] Available in various grades containing more or less naphthalene.

same price and finds almost exclusive application as a solvent. A complete list of the uses of these two distillates would be inordinately lengthy; the following are typical: as a general solvent for alkaloids, camphor, essential oils, fats, fixed oils, iodine, phosphorus, resins, rubber, sulfur; in the manufacture of brake linings, fan belts, waterproof fabric, transmission belts, oilcloth and linoleum, friction tape, adhesives, rubber cements, glue, printing inks, paints, enamels, lacquers and varnishes, paint and varnish removers, cleansing and degreasing agents, disinfectants, cosmetics and ceramics; in the dry-cleaning industry; and as a denaturant for alcohol.

Motor Benzol (Acid Washed). Although the distillation specifications allow the admixture of considerable quantities of toluene and xylene, the motor fuel prepared from coke-oven light oil is predominantly benzene. It is used in the petroleum industry to increase the anti-knock rating of natural or cracked gasolines and is admixed in quantities up to 50 percent. Because of the appreciable difference in specific gravities, benzol blends have higher heats of combustion per gallon than ordinary gasolines. Benzol fuels seem to have an actual engine-performance rating somewhat higher than that indicated by the test octane value. In order to meet an acid-wash specification, most of the valuable unsaturates are removed. Some refiners produce very thoroughly refined motor benzols. With the introduction of the inhibitor process, the manufacture of acid-washed motor fuel has become an anachronism.

Inhibited Motor Fuel. The preparation of this material is very simple, consisting usually of the addition of very small amounts of anti-oxidants to a crude benzol cut. If large amounts of carbon disulfide are present in the original charging stock,

a continuous forerunnings stripper may be necessary. It is generally recognized that this product is the equal in every way, for motor-fuel purposes, of acid-washed motor fuel. Practically all recent plants are designed to employ the inhibitor process.

As indicated above in the description of acid-washed motor benzol it seems to be definitely established that benzol-containing motor fuels have an actual engine-performance rating somewhat higher than that indicated by the test octane number. Evidence for this statement was given as early as 1934 in the results of the Uniontown Hill tests conducted by the Cooperative Fuel Research Group. The benzol blend used in these tests, a mixture of third-grade gasoline and motor benzol, showed in actual performance the highest positive deviation of any of the fuels from the A.S.T.M. octane rating. Benzol blends with an A.S.T.M. rating of only 68.1 octane units were found to have a hill rating of 70.8 octane units. The average difference, for all fuels, between the A.S.T.M. octane number and the hill-rating octane number was only 0.36 unit.[36]

In 1940, all types of motor benzol represented 0.40 percent of the total United States production of motor fuel.

Nitration Toluol and Industrial Pure Toluol. During wartime, the most significant chemical property of toluene is the formation with nitration· mixtures of 2,4,6-trinitrotoluene, a powerful explosive of convenient stability. The purest grades of toluol are required in the manufacture of this compound. As a raw material, toluol is also the starting point in the preparation of anthranilic acid, artificial musk, benzaldehyde, benzoic acid, benzyl chloride, β-methylanthraquinone, orthotoluenesulfonchloride, paraphenetidine, saccharine, toli-

36 Veal, C. B., *Oil Gas J.*, **33**, No. 27, 49–52 (1934).

dines, toluidines, and various dyes such as the triarylmethane colors. Toluol is employed as a solvent for alkaloids, cements, cellulose esters and ethers, dopes, enamels, lacquers, stains, varnishes, resins, rosin, and waxes; as an extractant for animal and vegetable oils; and as a degreasing agent for bone and hair. Significant quantities are used in the artificial leather, printing-ink, and oilcloth industries.[37] It is the most widely utilized hydrocarbon diluent in the lacquer trade.

The Xylols. Three-degree xylol (nitration xylol) is generally used as a chemical raw material; the other more widely boiling grades are employed as solvents. As a raw material, xylol is the starting point in the manufacture of mothproofing agents, pharmaceuticals, sulfonic acids, 2,4,6-trinitrometaxylene, xylyl bromide (a poison gas), xylene musk (perfumes), and various intermediates. Some of the solvent applications include acid-proofing, airplane dopes, aniline, azo dyes, carbazole, ceresin, cresol, enamels, lacquers, varnishes and paints, insecticidal compositions, maleic anhydride, naphthalene, plasticizers, resins, rubber cements, and sludge sulfonic acids. Industrial xylol is practically synonymous with refined solvent naphtha.

Refined Heavy Solvent. This category, the "hiflash naphthas," includes a variety of high-boiling solvents, all acid washed to remove polymerizable resins. A typical analysis as given by Downs [38] is shown at the top of the next column.

The high-flash naphthas are employed as slow-drying solvents; in the manufacture of ordinary enamels, house paints, and flat wall and interior paints; and in the printing-ink, shoe-polish, and linoleum indus-

COMPONENT	PERCENT BY WEIGHT
Ethyl benzene, xylene, cumene, propyl benzene, ethyl toluene	10
Trimethylbenzenes (largely pseudocumene)	45
Tetramethylbenzenes (largely isodurene)	40
Naphthalene	5

tries. Added to petroleum thinners, they increase the solvency of the thinners for natural and synthetic resins. The closed-cup flash point of these distillates is usually greater than 100° F.

Crude Light Solvent. This medium-boiling solvent is a straight-run distillate, not acid washed, having a deep straw color and containing a large percentage of unsaturated hydrocarbons, chiefly styrene. It is a relatively unexploited source of styrene as a raw material in resin manufacture. As a solvent, it finds application where the odor and color can be tolerated, as in "rubber solutions, bituminous paints, type and roll cleaners, insulating varnish thinner, wire enamels, paint and varnish removers, brake lining and fabric belt saturation and in the preparation of cold patch bituminous materials for repairing roads." [38]

Crude Heavy Solvent. Manufactured to varying specifications, the crude solvents are highly colored (deep amber to dark red), high-boiling, strongly unsaturated distillates. A typical composition could be as follows:

COMPONENT	PERCENT BY WEIGHT
Coumarone, indene	60
Hiflash naphtha components	20
Methyl naphthalenes and naphthalene	20

They are employed in the preparation of dark-colored paints, bituminous paints and enamels, wire enamels, asbestos board, brake lining, pipe coatings, shingle stains,

[37] Gregory, T. C., *Uses and Applications of Chemicals and Related Materials*, Reinhold Publishing Corp., New York, 1939, 665 pp.

[38] Downs, C. R., *J. Soc. Chem. Ind.*, **51**, 45–9 (1932).

and ship-bottom paints. Extensive use in the manufacture of wire enamel has led to the adoption of such polyonymics as "wire-enamel solvent" and "heavy solvent E-W."

As a chemical raw material, crude heavy solvent is used in the manufacture of the many grades of paracoumarone-indene resins. For this purpose a close-cut distillate boiling from 160 to 190° C is usually employed. Further refining may consist of a weak acid wash for dehydration and the removal of undesirable reactive hydrocarbon constituents. Polymerization is carried out by vigorous agitation with small quantities (0.2 to 1.0 percent) of 66° Baumé sulfuric acid. Acid tars are quickly separated and the residual oil is neutralized, water-washed, and steam-distilled to leave the resin product as a residue. Although these resins can be made initially almost colorless, their usefulness is restricted by their undependable color stability. The yellowing of paracoumarone-indene resins has been ascribed to self-fulvenation and may be greatly reduced by hydrogenation.[39]

Coumarone resins are widely used in the manufacture of printing inks, waterproofing materials, rubber compositions, varnishes, linoleum, flooring and floor tile, and chewing gum.[35]

THE FORMATION OF LIGHT OIL

As most of the coal carbonization in this country is carried out in conjunction with steel manufacture, oven design and carbonization conditions are adjusted chiefly to the production of a good quality of blast-furnace or foundry coke. A considerably smaller, but steadily increasing, amount of coal is carbonized at coke ovens operated by gas plants; here design and operating

39 Carmody, W. H., *Ind. Eng. Chem.*, **32**, 525–7 (1940). Carmody, W. H., Kelly, H. E., and Sheehan, W., *ibid.*, **32**, 684–92 (1940). Carmody, W. H., and Kelly, H. E., *ibid.*, **32**, 771–5 (1940).

procedures are directed to the manufacture of a suitable public-utility gas and furnace or "domestic" coke of proper combustion characteristics. Light-oil credits, like other byproduct credits, play a subordinate part in coke-oven economics, and the fundamental design of batteries usually places emphasis on other considerations. Compromises must be found between the relative desirability of securing a maximum yield of byproducts and of producing a high-temperature coke uniformly heated, with the use of a minimum amount of heat for underfiring. The flexibility in constructional design of the standard modern low-differential underjet oven is such that, given all economic and physical variables, an admirable compromise meeting all local conditions can usually be achieved.[28] In America, the inclusion of special structures to increase the yield of light oil is not feasible economically and is not practiced; conversely, the economic situation in Europe has led to the limited use of a wide variety of such devices. The plant-scale data so obtained are interesting from the standpoint of implementing current speculations concerning the mechanism of the formation of light oil during the coking of coal.

The carbonization process has been adequately described elsewhere in this treatise; only a few details germane to this discussion will be presented here. On charging, or filling the oven chamber, a uniform layer of cold, crushed coal is deposited between two very hot vertical walls closed with gas-tight doors on each end. The coal adjacent to the walls rises rapidly in temperature; up to 350° C the principal products are occluded gases, and water and carbon dioxide resulting from internal condensation. At this point (300 to 400° C) the coal softens and the well-known plastic layer is formed. Significant breakdown of the molecular structure of the coal does not

occur until this temperature is reached and exceeded. The primary condensable products formed by the decomposition of the plastic layer are chiefly hydroaromatic compounds together with smaller proportions of the higher olefins, paraffins, and phenolic compounds. At the point of origin aromatic compounds of the benzene series are found only in negligible quantities. As carbonization proceeds, the plastic zones slowly move away from the walls and eventually meet in the center of the charge.

The plastic layer has considerable mechanical strength or impermeability, and most of the primary products find their way out of the oven by traveling toward the wall through the hot coke and then upwards along the hot wall, finally passing through the highly heated free space above the charge. Some of the gases escape through the unheated central portion of the coal, particularly when uncrushed or run-of-mine coal is used; when this happens the plastic zones are not well defined and a larger proportion of the gas finds its way through the cold coal. The light oil in the gas entering the collecting main is strikingly different from the light oil in the primary distillation products, and its nature depends largely upon the extent to which secondary thermal decomposition takes place. The completeness of the secondary heat treatment in turn depends upon a variety of factors some of which are: (1) the proportion of gas which escapes up the center core of raw coal; (2) the temperature of the walls; (3) the temperature of the free space above the coal charge; and (4) the time of contact of the gas in the hot free space.[40]

These factors vary widely with different carbonization systems, and the extent to which they are operative goes far to characterize the light oil produced. Combined,

they define the maximum temperature to which the primary decomposition products are heated in the oven. Extensive pyrolysis studies on the pure aromatics have been made,[41] but the results cannot well be extrapolated to the complex atmosphere of the oven charge or free space. Practically, it is found that the maximum yield of purely aromatic hydrocarbons is obtained when the products of distillation are heated to a temperature of about 850° C. Below this point excessive quantities of paraffins or naphthenes appear; at higher temperatures considerable cracking of the aromatics to higher-boiling compounds occurs. The optimum, eventual, nitration toluol yield is particularly sensitive to thermal conditions since the amount of nonnitratable material that can be tolerated is strictly limited. Assuming the equivalence of all other variables, carbonization time is approximately inversely proportional to wall temperatures, and the above statements concerning the composition of light oil can be expressed in terms of the length of the coking period.

Tweedy has reported as follows for silica regenerative batteries operating with the same coal: [42]

Carbonizing time, hours	29.5	18.6	15.1
Benzol, percent by volume	64.9	79.0	86.1
Toluol	25.3	18.3	12.2
Solvent naphtha	8.8	2.2	1.5
Paraffins up to 140° C	1.1	0.5	0.2

Many of the inventions later described are designed to make the yield and quality of the light oil substantially independent of coking times, which must often be chosen without regard to the effect on the composition of the light oil.

As would be expected, the evolution of

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[40] See p. 45 of ref. 6.

[41] Egloff, G., *The Reactions of Pure Hydrocarbons*, Reinhold Publishing Corp., New York, 1937, 897 pp.

[42] Tweedy, S., *Gas World*, **94**, No. 2427, Coking Sect., 15-8 (1931).

light oil is not uniform throughout the coking period. Quantitative data for a particular instance have been supplied by Saunders and Smith.[43] A good quality of Durham (English) coking coal was carbonized in a 16-inch coke oven operating with an average flue temperature of 1440° C and a coking time of 14 hours. Samples of the distillation products were withdrawn periodically from the ascension pipe and were

TABLE VI

LIGHT-OIL YIELD AND COMPOSITION AS A FUNCTION OF THE PROGRESS OF CARBONIZATION [43]

Oven Age	Light Oil	Benzol	Inches of Charge above 700° C
hours	grams per cubic meter	percent	
0	....	....	0
1	21.1	69.5	3.8
2	26.7	71.9	6.0
3	29.5	74.2	7.2
4	30.1	76.7	8.2
5	28.8	79.4	9.0
6	27.2	82.5	9.6
7	25.4	85.9	10.0
8	23.2	89.3	10.4
9	20.7	93.7	10.8
10	17.6	97.4	11.2
11	13.1	97.4	13.0
12	3.4	....	....
13	....	....	....
14	....	....	....

characterized by the analyses shown in Table VI.

A detailed discussion of the mechanism of formation of sulfur compounds in coke-oven gas is found in Chapter 26. Of these compounds, thiophene (C_4H_4S, b.p. 85° C) is the most difficult to remove from light oil. It has been suggested that the discovery of the formation mechanism of thiophene might lead to a fundamental solution

of the refining problem based on either inhibition of the formation of this compound or its conversion to some more easily removable form of sulfur.[44]

INCREASING LIGHT-OIL YIELDS

Much inventive effort, especially in foreign practice, has been applied to the problem of increasing the yield and improving the quality of coke-oven light oil. Most of these attempts, with a variety of success, have depended on pretreatment of the coal, changes in the conventional method of withdrawing gaseous byproducts from the oven, and modification of the heat treatment in the free space through the incorporation of special channels, ducts, and chambers in the oven structure.

Pretreatment of the Coal. The sulfur compounds in coke-oven gas are very roughly proportional to the sulfur content of the coal; washing high-sulfur coals to remove sulfur-bearing ash will be reflected in a lower sulfur content of the light oil. To insure uniform operation the degree of pulverization and the moisture content of the mixed coals should also be well controlled.

Frequently, at coke ovens operated at gasworks, the allowable extent of light-oil recovery is governed by statutory or contractual specifications for the specific gravity of the send-out gas. Light-oil yields may then be increased by the application of small quantities of heavy oil to the crushed coal. The increased yields are partly due to an increased light-oil content of the gas; more important is the fact that the incremental increase in density of the gas permits the use of total scrubbing. The increase in density of the gas is due directly to the high density of the oil gas and indirectly to the fact that the large heat content of the oil gas allows dilution

[43] Saunders, S. W., and Smith, F. F., *ibid.*, 98, No. 2539, 40–3 (1933).

[44] See p. 53 of ref. 6.

with a larger quantity of high-density producer gas. Modern techniques in the use of oil on coal have been described by Ramsburg and McGurl.[45]

Special Methods of Gas Withdrawal. A typical scheme is the Still process practiced on a limited scale in Germany.[46] One form involves the formation of about ten vertical holes in the top surface of the coal charge. Gas collecting tubes are placed in these holes in the oven contents and suitably connected to a special gas collecting main, the "inner gas" main. By appropriate adjustment of the pressures in the "inner gas" and "outer gas" (regular) collecting mains a varying proportion of the primary distillate can be forced to pass through the cool uncoked portion of the charge. In this way an increase in light-oil yields of about 10 percent can be demonstrated. Unfortunately, the incremental light oil, since it is of comparatively low-temperature origin, contains very large quantities of paraffinic and naphthenic compounds. Still-process light oil is chiefly utilized as a motor fuel.

Similar in purpose is the system described by Niggemann.[47] Here the "inner gas" offtake ducts protrude through the oven side doors. The light-oil content of the gas is decreased, but this loss is more than made up by the increase in the light-oil fraction distillable from the tar.

Modified Heat Treatment in the Free Space. The gaseous byproducts of coal distillation reach their highest temperatures in the free space above the charge. A variety of schemes have been used to control the intensiveness of the thermal decomposition at this point. Best known are the Goldschmidt[48] and Stöter-Tillman[49] channels which have found a limited use in Germany and England.

The Goldschmidt channel consists of a horizontal duct integrally incorporated in the relatively cool brickwork of the oven top and connected to the free space at a large number of points by a series of orifices of varying sizes. The Goldschmidt channel is in turn connected in the usual way to the ascension pipe. The time of exposure of the gases to the intensely heated walls of the free space is considerably shortened since the major portion of the exit path is through a duct some 200° C cooler than the free space. An increase in light-oil yields of about 10 percent has been claimed; the figure depends greatly upon the type of coal, the length of the carbonizing period, etc. Sometimes no beneficial effect can be observed.[50] Wilson[51] reported that, for the very high coking rates of about 1½ inches per hour, there is a very definite increase in light-oil yield and that the results on the whole can be considered very satisfactory. This writer further notes that the use of high carbonizing rates (1 inch per hour or more) may

45 Ramsburg, C. J., and McGurl, G. V., *Proc. Am. Gas Assoc.*, **1940**, 666-78.

46 Still, C., U. S. Pats. 1,810,629 (1931), 1,-937,853, 1,940,562, 1,940,567 (1933), 1,946,721, 1,943,562 (1934), 2,030,334, 2,065,963 (1936), 2,066,704 (1937). Dean, H., *Fuel*, **13**, 112-5 (1934). Nettlenbusch, L., and Jenkner, A., *Glückauf*, **70**, 1165-72 (1934). Thau, A., *Brennstoff-Chem.*, **15**, 41-5 (1934). Foxwell, G. E., *Gas World*, **102**, 415 (1935). Anon., *Gas- u. Wasserfach*, **79**, 24-5 (1936).

47 Niggemann, H., *Glückauf*, **73**, 705-11 (1937); *Z. Ver. deut. Ing.*, **82**, 43-4 (1938); Ger. Pats. 658,299, 662,645, 663,668, 664,832, 667,125 (1938).

48 Goldschmidt, F., Brit. Pat. 391,726 (1933); Ger. Pat. 614,310 (1935). Warwick, W. N., Brit. Pat. 450,346 (1935).

49 Stöter-Tillman, H., Brit. Pat. 392,496 (1933); French Pat. 752,432 (1933); Ger. Pat. 611,670, 623,493 (1935). Busch, W., Colin, A., and Schmitz, H., *Glückauf*, **69**, 490-3 (1933).

50 Litterscheidt, W., and Reerink, W., *Glückauf*, **71**, 461-71 (1935).

51 Wilson, O. B., *Gas World*, **27**, No. 325, Coking Sect., 9 (1940).

lead to the obstruction of the channel with soot. Goldschmidt light oil, like Still-process oil, contains somewhat higher concentrations of the paraffinic and naphthenic compounds than are found in regular high-temperature coke-oven light oil.

In the Otto [52] system an essentially similar result is obtained in a distinctly simpler manner. In addition to the usual collecting main, all the ovens are connected to the supplementary compensating Beimann main, which is not directly connected to the byproduct system but serves only to interconnect the oven chambers. By a proper equalization of pressures, the distillation products from a green oven can be forced to flow through the free space of an older or more coked-out oven. In this way there results a general overall reduction in the temperature of the free space and the light oil is poorer in benzene and richer in toluene.[51] Increases in yield of 15 percent have been reported,[53] but the effectiveness of the system seems to depend greatly upon the particular coal used.

Somewhat more elaborate than the above are proposals involving the passage of the distillation products through heated chambers containing catalysts,[54] and the provision of special flues or brickwork where the gases can either be heated or cooled as desired.[55] It has been claimed that high-temperature light oils can be produced in low-temperature carbonization processes by the introduction into the free space of enough air to raise the temperature to 850° C.[56]

[52] Otto & Co. G.m.b.H., Brit. Pat. 460,509 (1935).
[53] Brückner, H., *Handbuch der Gasindustrie*, Oldenbourg, Berlin, 1938, Vol. III, p. 119.
[54] Reppekus, W., U. S. Pat. 2,116,641 (1938).
[55] Concordia-Bergbau A.-G., Brit. Pat. 419,125 (1934). Hinselmann Koksofenbauges. m.b.H., Brit. Pat. 482,399 (1934).
[56] Koppers, H., U. S. Pat. 2,194,859 (1940).

The Recovery of Light Oil

The profitable recovery of light oils from high-temperature coke-oven gas presents a chemical-engineering problem of only slight difficulty. The most relevant factors affecting design are: (1) the components to be removed make up only 1 percent of the gas to be handled; (2) the gas is approximately only 10 percent saturated with the vapors of the chief light-oil components—benzene, toluene, and xylene; (3) the light-oil components are relatively inert chemically; and (4) the gas, except in isolated cases, is usually unpurified and contains tar fog, hydrogen sulfide, traces of ammonia, etc.

For simplification of plant processes and the avoidance of corrosion troubles it is usually found that removal of light oil is made the last step in any byproduct-recovery system. At gas plants, intensive purification of the gas is practiced, particularly with reference to hydrogen sulfide. The light-oil plant may then be operated with the minimum of difficulty and the subsequent refining processes are substantially simplified. At coke ovens operated in conjunction with steel plants, gas purification is usually limited to tar and ammonia removal of varying degrees of completeness. The removal of sulfur compounds is not generally practiced, although a few plants utilize the hydrogen sulfide in the gas as a raw material in the manufacture of sulfuric acid.

In contrast to the conventional procedure of placing the light-oil plant after ammonia recovery, Schmalenbach [57] and Still [58] proposed the simultaneous recovery of light oil and ammonia.

In the widely used semi-direct ammonia-recovery process the temperature of the gas leaving the ammonium sulfate satu-

[57] Schmalenbach, A., U. S. Pat. 2,135,356 (1938).
[58] Still, C., Ger. Pat. 603,295 (1934).

rators is about 60° C. Inasmuch as the wash-oil process of light-oil recovery functions most effectively at temperatures considerably lower than this (15 to 25° C), the provision of some type of gas cooler is mandatory. Of the many possible types, the simple direct system consisting of a vertical, cylindrical shell filled with widely spaced wooden grids is most widely used. Injected through suitable spray devices at the top of the tower, the cooling water comes in direct, countercurrent scrubbing contact with the upward-flowing warm gas. Considerable naphthalene and, on occasion, some of the "heavy solvent" components of light oil are thereby removed, the amounts depending upon the temperature of the cooling water and whether or not the water is recirculated. Seasonal variations in the composition of light-oil production may often be correlated with final cooler operation.

The rather short history, chronologically speaking, of the light-oil industry has seen the development of a large variety of recovery processes based on both chemical and physical principles. Only the physical principles are now employed; they can be discussed in three categories: (1) simple condensation involving no absorbent media; (2) condensation on the surface of solid adsorbents; and (3) condensation in liquid absorbents.

SIMPLE CONDENSATION INVOLVING NO ABSORBENT MEDIA

In this class are methods involving simple cooling, simple compression, or suitable combinations of the two. These processes are attractive in that light oil is directly obtained and the regeneration of absorbent media is completely avoided. Light oil starts to condense, at atmospheric pressure, from coke-oven gas at −20° C; to obtain satisfactory removal the tempera-

ture must, however, be lowered to about −70° C. In the same way, using compression at normal temperatures, light oil starts to condense at approximately 10 atmospheres. Because of the large volumes involved the only practical application of these principles utilizes simultaneous compression and refrigeration. Although not found in America, such plants are operated abroad, usually prior to the recovery of pure hydrogen from coke-oven gas for use as a raw material in ammonia synthesis.[59] In such plants extensive refrigeration equipment is already involved, and it is economical to utilize the same principle in light-oil recovery. A multistage process [60] is convenient since it is desirable to remove the naphthalene and water in a preliminary treatment of relatively mild cooling and refrigeration. The separation of solid benzene "snow" leads to mechanical difficulties and may be avoided by means of added hydrocarbons [61] or mitigated by rotating scrapers, etc.[62]

The advantages of the process are eclipsed by its chief disadvantages: the high cost of the specialized equipment and plant; high maintenance and labor charges; and the significant power requirement necessary in the cooling and compressing of large quantities of comparatively lean coke-oven gas. More feasible would be the application to light-oil recovery from low-temperature carbonization, since the gas volumes are then relatively small.

As mentioned above, the principles of refrigeration and cooling are applied to the recovery of light oil only in connection

[59] Thau, A., *Gas- u. Wasserfach*, **73**, 717–21 (1930).

[60] Kemmer, H., Brit. Pat. 370,243 (1931).

[61] Burlachenko, G. O., *Coke and Chem. (U.S. S.R.)*, **1938**, No. 12, 27–80. Maiuri, G., U. S. Pat. 2,219,782 (1940).

[62] Aguillon, J. E., Brit. Pat. 210,114 (1922). La société des hauts fourneaux de Rouen, Ger. Pat. 389,774 (1922).

with ammonia-synthesis plants. European practice has been described by Wucherer.[63]

SOLID ADSORBENTS

It has long been known that solid surfaces have the ability of adsorbing small amounts of gases and vapors. A technically useful adsorbent presents a very large surface area per unit volume: substances like iron oxide gel, silica gel, zeolites, and active carbons or charcoals fall in this class.

Many utilizations of adsorbent processes are known, but only recently have they been successfully applied to light-oil recovery. In the pioneering development it was found that the chief difficulty lay in the then notoriously short working life of the active carbon, this adsorbent alone proving practical. Through a systematic investigation by Hollings and associates [8] of the role played in carbon deterioration by the various components of coal gas, the working cycle has been lengthened to such an extent that the process now can actively compete, in foreign technology, with the older well-known wash-oil process. In the United States, large quantities of excellent absorbent oils are available at such low prices that there has been little interest in other methods and no active-carbon installations have been made. In addition, the process is peculiarly suitable for gas plants where, under American conditions, light-oil recovery has not usually been feasible. In contrast, the lack of a good indigenous petroleum wash oil has led to the widespread utilization of active-carbon processes in foreign practice, particularly in Germany, France, and Switzerland. Of the few installations in England, the Beckton plant of the London Gas Light and Coke Company, which produces 24,000 U. S. gallons

of light oil per day, is perhaps the largest active-carbon plant in the world.

In its simplest outlines, an active-carbon light-oil-recovery plant is operated as an intermittent two-stage process consisting of an adsorbing and a stripping step. ·The light oil is removed from the gas by passage of the gas through a bed of active carbon suitably disposed in a large vessel. Recovery is almost quantitative until the "break point" is reached, at which the efficiency of removal drops off very rapidly. At this point the flow of gas is interrupted and diverted into a fresh adsorber. The saturated adsorber is suitably connected with condensing equipment, and the light oil is driven from the carbon by means of both indirect and direct steam. After cooling, usually accomplished by circulating water through coils embedded in the carbon, the adsorber is again ready for light-oil recovery, and the cycle is resumed. The carbon gradually loses its effectiveness through the deposition of resinous material within the pores and must be discarded after approximately 1,200 to 1,500 repetitions of the adsorption and stripping cycle. A detailed description of the operation of the Beckton plant of the London Gas Light and Coke Company has been given by Hoffert and Claxton.[6] A diagrammatic layout of this plant is shown in Fig. 2.

The actual mechanism of vapor adsorption on active carbon is not known. It is reasonable to assume that the molecules of the solid lying in the outer surface, because of their unique position, display a reactivity that can be interpreted in terms of chemical valences. Entanglement of the vapor will hence produce a strongly held monomolecular layer of the adsorbed material. It is also probable that such bound molecules display similar entangling properties, and the process may continue until

63 Wucherer, J., *Gas. u. Wasserfach,* **78,** 118–21 (1935) ; *Stahl u. Eisen,* **58,** 689–92 (1938) ; *Gas World,* **109,** 299–301 (1938).

the layer is several molecules thick A mechanism of this sort would account for the selective type of phenomena exhibited by active carbons and would explain adsorption on smooth surfaces

is, theoretically, an inverse function of the capillary diameter, and by postulating sufficiently small dimensions the observed reduction in vapor pressure of adsorbed liquids can be explained In such a mecha-

STRIPPED GAS OUTLET

TURBINE EXHAUST STEAM INLET 5 LB/□″

LIVE STEAM INLET 200 LB/□″

BENZOLE TO STORAGE

WASTE WATER TO DRAIN

RICH GAS INLET

1 ADSORBERS	9 CONDENSED STEAM TANK
2 CONDENSERS	10 STEAM METER
3 PRELIMINARY SEPARATORS	I REDUCING VALVE
4 FINAL SEPARATORS	12 GAS COOLERS
5 V S BLE OVERFLOW	13 4 WATER COOLERS
6 BENZOLE METERS	15 16 17 WATER PUMPS
7 STEAM EVAPORATORS	
8 SUPERHEATERS	

RICH GAS & STRIPPED GAS
HIGH PRESSURE STEAM 200 LB/□
LOW PRESSURE STEAM FOR COILS 60 LB/□″
COOLING WATER
CONDENSED STEAM (FEEDING EVAPORATORS)
BENZOLE & BENZOLE VAPOUR STEAM MIXTURE
STEAM FOR FLUSHING ADSORBERS 5 LB/□″

Fig 2 Flow diagram of the Beckton active carbon light oil recovery plant of the Gas Light and Coke Company London [6]

In porous materials the total amount of adsorption that takes place is very great compared to the actual surface available, and the calculated thickness of the polymolecular layer becomes unreasonably large A portion of the observed phenomenon is ascribed to simple condensation in fine capillary tubes or between closely adjacent laminar structures The difference between the vapor pressure of a condensed liquid in a capillary and the normal vapor pressure

nism the extent of adsorption depends only on the physical properties of the material and the diameter of the capillaries and is non-selective Adsorption on silica gel and zeolites seems to be predominantly of this type The adsorption mechanism of light oil on active carbon can best be attributed, in the present state of knowledge, to an indeterminate combination of these two effects

It has been found that the Freundlich

equation,[64] a simple power function, holds quite well for the adsorption of light oil on the carbons now used for the purpose. At any one temperature, the relation between x, the amount of light oil adsorbed, and p, the vapor pressure of the light oil in the gas, is

$$x = ap^N$$

where a and N are constants depending upon the temperature, the type of carbon, the history of the carbon, and the nature of the light oil. N is substantially independent of temperature; da/dT is about 0.01 per °C at 15° C. In practice it is desirable that the adsorption per gram of carbon be as large as possible; this is accomplished by using reactive carbons and reasonably low temperatures (high a). In order that the effectiveness of adsorption will not suffer at low concentrations it is desirable to choose carbons characterized by low values of the constant N.[65]

In addition to light oil, considerable amounts of the other components of coal gas are adsorbed, and significant quantities find their way into the light oil. Light oil recovered from active carbon contains larger quantities of ammonia, nitric oxide, cyanogen, carbon oxysulfide, hydrogen sulfide, carbon disulfide, and light unsaturated hydrocarbons, particularly the last two, than does that recovered from wash oil.

As coal gas is passed into a freshly steamed absorber, the carbon becomes progressively saturated, first with the more-volatile materials, then with the higher-boiling compounds such as benzene, toluene, etc. Eventually considerable quantities of the lighter materials first adsorbed are dis-

placed by the less-volatile components of light oil. If quantitative removal of the carbon disulfide is desired, it is found that the adsorber must be removed from operation when only two-thirds saturated with light oils.[66]

Some of these adsorbed materials profoundly affect the efficiency and life of the carbon. Hydrogen sulfide is oxidized by the small amount of oxygen usually present in coal gas, the carbon acting as a catalyst, and the resultant deposit of sulfur soon greatly reduces the effective surface area of the carbon. Gas free from hydrogen sulfide is an axiomatic requisite for economic application of the process, and the recovery plant is usually placed after the dry box purification system. The removal of naphthalene from the gas before light-oil recovery is usual in British practice and is thought desirable, especially in large installations; this precaution is dispensed with in certain continental installations.

The most serious, and at present unsolved, deterioration of the carbon results from the deposition of a low-volatile gum or resin in the pores of the adsorbent. There is considerable evidence to show that this material is the result of some reaction between the hydrogen cyanide in the gas and some of the unsaturated constituents of light oil. Although the nitrogen content of the gum is small it is not believed that the action of the hydrogen cyanide is purely and wholly catalytic. The extent of formation of the resin seems to depend on a variety of factors, including the relative directions of gas and steam flow, the bed temperature during adsorption, the length of time light oil is allowed to remain in the carbon filter before removal by distillation, and the thermal conditions during this distillation. The deterioration of carbon

64 Freundlich, H., *Kapillarchemie*, Akad. Verlagsgesellschaft m.b.H., Leipzig, 2nd ed., 1920, 591 pp.

65 Fellmann, H., *Schweiz. Ver. Gas- u. Wasserfach. Monats-Bull.*, 20, 52–62, 71–80, 87–95, 102–7 (1940).

66 Blume, K., *Gas- u. Wasserfach*, 78, 785–9, 810–4 (1935).

through gum deposition is not akin to the poisoning of catalysts where only minute traces of impurities are involved but seems to be chiefly a mechanical effect; the amount of gum finally adsorbed may be 25 to 30 percent of the original carbon weight. Further, the adsorptive capacity of the carbon for gum is greater than the initial adsorptive capacity for light oil. In practice, it is found that the rate of deposition of resin may be significantly decreased by a proper combination of empirical operating techniques which include:

1. Countercurrent directions of flow for gas and steam in the adsorption and stripping steps. In comparison with concurrent flow it is relatively more difficult for light-oil constituents of high molecular weight to penetrate far into the charcoal bed.

2. The avoidance of excessive rise in temperature of the adsorbent during both adsorption and stripping. Temperature control during stripping is easy; temperature control during adsorption is profoundly affected by the amount of water retained by the carbon in the stripping step. During adsorption, 600 to 700 Btu of heat per pound of light oil is evolved and dissipated through radiation, increase in sensible heat content of the outlet gas, transfer to cooling water circulated in embedded coils, vaporization of water in the carbon, and rise in temperature of the adsorbent. Heat removal by the evaporation of water is predominant, especially in the early stages of adsorption, and careful control of the residual moisture content of the bed is necessary for economic operation.

3. Saturated adsorbers should be steamed immediately on removal from the line; that is, the time of contact of light oil on hot carbon should be held to a minimum.

4. During adsorption, gas should not be allowed to pass through the filter after the break point is reached.

Observation of the appearance of a flame is a sensitive control procedure. Beyond the break point the efficiency of light-oil recovery drops precipitously to uneconomic levels while the efficiency of gum adsorption seems quite unimpaired.

The active carbon must be periodically replaced since no good regeneration procedure exists. Extraction with solvents is a practical failure, as the best solvent, pyridine, will remove only about one-fourth of the gum. Partial regeneration can be accomplished by strong heating in inert atmospheres and by hydrogenation processes, typical of which is a method involving treatment with aqueous ammonium vanadate and hydrogenating at 440 to 450° C under a pressure of 250 to 280 atmospheres.

In contrast to active carbon the reactification of silica gel is relatively easy and can be accomplished by heating to 550 to 600° C in an oxidizing atmosphere. Gums are burned away with no appreciable deterioration of the adsorbent macrostructure. Although silica gel is an active adsorbent for light oils its hydrophilic nature necessitates a somewhat more complicated mode of operation. The steam stripping process leaves the silica gel bed in a condition unfavorable for light-oil adsorption; it must be followed by procedures designed to dry the gel completely. A hydrophobic material, such as active carbon, is evidently superior, since simpler processes can be used. No plant-scale commercial installation of silica gel light-oil recovery was ever made. Semi-large-scale experiments carried out in 1923 by the Silica Gel Corporation resulted in a pilot plant of novel design. The process was continuous, adsorption, stripping, and drying taking place in a countercurrent flow of levigated silica gel with gas, steam, and hot air.[67] Soon aban-

67 Williams, E. C., *J. Soc. Chem. Ind.*, **43**, 97-112T (1924).

doned, this plant is historically interesting in that it represents the solitary example of the utilization of solid adsorbents for light-oil recovery in America. The American coke-oven operator's preference for the wash-oil process can be explained through a comparison of the advantages and disadvantages of the two processes.

The advantages of the active-carbon over the wash-oil process are as follows: (1) for equal percentage extraction efficiencies the consumption of process and heating steam is slightly less in the active-carbon process; (2) power and cooling water requirements for the active-carbon process are less than those required in the oil-absorption system; (3) the operation of solid adsorbent methods of light-oil recovery can be practiced with relatively high gas temperatures with only slight loss of recovery efficiency; (4) the light oil is not contaminated with an absorbent material, e.g., wash oil; and (5) in normal operation the active-carbon process will remove 70 percent of the sulfur compounds in the gas as compared with the 40 to 60 percent removal usually achieved in the wash-oil recovery process.

These advantages are more than outweighed, especially in American practice, by an imposing list of disadvantages: (1) the replacement cost, per gallon of light oil, of active carbon is many times that of a good petroleum wash oil; (2) hydrogen sulfide must be removed from the gas, while most large American light-oil-recovery plants are operated at steel plants where desulfurization of the gas would not be otherwise necessary; (3) corrosion of adsorbers and other equipment is intensive; (4) the intermittent nature of the process inevitably results in increased labor, control, and supervision; and (5) the crude benzol or motor-fuel cut of active-carbon light oil will contain nearly twice as much sulfur as the similar fraction of wash-oil-process light oil and will require more expensive refining techniques. At plants using low-sulfur American coals and a wash-oil process it frequently happens that simple fractionation (no forerunnings stripper) of the light oil produces a motor benzol well under current sulfur specifications. This would rarely, if ever, result if a solid-adsorbent process were employed.

The continental applications of the active-carbon process are quite similar to the British practice described in detail above except that the preliminary oil wash to remove naphthalene, indene, and coumarone is frequently omitted. Many descriptions are available in the technical literature.[68]

LIQUID ABSORBENTS

All American light oil and the bulk of foreign light oil is recovered by some variation of the traditional liquid absorbent system. Basically, two steps are always involved: (1) washing the rich gas with a suitable liquid menstruum; (2) stripping the absorbed hydrocarbons from the enriched *wash oil* and condensing these stripped vapors to form light oil. Within

[68] Engelhardt, A., *Gas- u. Wasserfach*, **64**, 205–6 (1921), **65**, 473–7 (1922) ; *J. usines gaz*, **45**, 170–1 (1921). Urbain, E., *Gas J.*, **167**, 449 (1924) ; *J. usines gaz*, **49**, 1 (1925) ; *Chimie & industrie*, Special No., 245–51 (1925). Thau, A., *Gas World*, **83**, Coking Sect., 107 (1925). Reisemann, E., *Brennstoff Chem.*, **11**, 226–9 (1930). Engelhardt, A., and Rüping, H., *Gas- u. Wasserfach*, **76**, 478–84 (1933) ; *Gas J.*, **203**, 154 (1933). Plenz, F., *Gas- u. Wasserfach*, **77**, 457–62 (1934). Schon, V., *Montan Rundschau*, **28**, No. 22, 5–8 (1936) ; *Petroleum Z.*, **32**, No. 45, 13–6 (1936). Simon, A., *Gas- u. Wasser fach*, **79**, 857–62 (1936). Thoma, M., *Schweiz. Ver. Gas- u. Wasserfach. Monats-Bull.*, **16**, 257–68 (1936). Bunte, K., and Brückner, H., *Gas- u. Wasserfach*, **80**, 711–6 (1937). Schon, G., *Szénkisérleti Közlemények*, **3**, 148–54 (1937). Bailleul, G., Herbert, W., and Reisemann, E., *Aktive Kohle und ihre Verwendung in der chemischen Industrie*, F. Enke, Stuttgart, 2nd ed., 1937, 120 pp.

this fundamental framework the designer may vary the details of the process to suit local conditions. Thus there are plants operating with widely different types of wash oils, absorbing equipment, stripping equipment, etc. Even more important is the sensitivity of recovery efficiency to operating variables and the consequent flexibility inherent in any fixed installation. The simplicity of the equipment needed, the readiness with which a continuous process may be controlled, and the availability and cheapness in America of good petroleum wash oils all combine to make this system of recovery especially attractive to American operators.

Theoretical Considerations. Gas scrubbing is usually carried out countercurrently in vertical packed towers. A suitably cooled and purified coke-oven gas is caused to flow upwards through the packing material where it meets, and comes into more or less intimate contact with, a stream of absorbent oil flowing in the opposite direction. The efficiency of recovery for any one constituent will depend, in part, upon the relative proportions of gas and liquid, the nature of the constituent, the nature of the wash oil, the degree to which equilibrium between gas and liquid is attained, the temperature, and the detailed properties of the system: constituent-wash oil.

The treatment is much simplified and sufficiently accurate for all practical purposes if we assume that the partial pressure p of any constituent of light oil in the gas, such as benzene, is proportional to the concentration Y expressed in stoichiometric units (pounds of benzene per pound of lean gas). Similarly the concentration X of the constituent in the wash oil may be expressed in stoichiometric units (pounds of benzene per pound of wash oil).[69] The

low concentrations met with in light-oil-recovery practice fully justify these simplifications. It has further been found that, at normal scrubbing temperatures and at the low concentrations employed, the equilibrium data for the system can be adequately expressed by the stoichiometric form of Henry's law: [70]

$$Y = mX \qquad (1)$$

For American petroleum oils from one source, the constant m seems to be substantially independent of the molecular weight of the wash oil.[71] The deviations from Raoult's law almost exactly nullify any expected change with variation in molecular weight. Lacking an experimental determination, m may be computed from Raoult's law by taking the "apparent molecular weight" of American wash oils to be 260.

If L and G are the liquid and gas flow rates and the subscripts o and i refer to outlet and inlet conditions, a material balance across the absorption equipment gives the expression

$$\frac{L}{G} = \frac{Y_i - Y_o}{X_o - X_i} \qquad (2)$$

The maximum absorption will occur when the exit lean gas Y_o is in equilibrium with the inlet wash oil containing X_i of benzene. In the same way the minimum amount of wash oil necessary for the maximum absorption is found by assuming equilibrium at the bottom of the tower. By substitution of equation 1 in equation 2 the minimum critical oil-to-gas ratio is found to be

$$\frac{L}{G} = \frac{mX_o - mX_i}{X_o - X_i} = m$$

69 Sherwood, T. K., *Absorption and Extraction*, McGraw-Hill Book Co., New York, 1937, 278 pp.

70 Meier-Grolman, F. W., Oppelt, S., and Schmitt, H., *Oel Kohle*, **36**, 457–69 (1940).

71 Wilson, R. D., and Davis, H. S., *Ind. Eng. Chem.*, **15**, 947–50 (1923). Powell, A. R., *Proc. Am. Gas Assoc.*, **1935**, 699.

In other words, *for maximum absorption the necessary oil-to-gas ratio is independent of the concentration of the constituent in the gas*. It depends only upon *m*, which in turn varies with the vapor pressure of the pure constituent under consideration and the temperature. With an ordinary petroleum wash oil and operating temperature of 15° C, it is found that the critical ratio for benzene is about 6 gallons of wash oil per 1,000 cubic feet of gas. The critical ratios for the less-volatile components are considerably smaller; if an oil-to-gas ratio adequate to absorb benzene completely is chosen, the maximum absorption of toluene and xylene is automatically assured. The possible absorption may not be complete since the degree of debenzolization is an important variable. Complete debenzolization in the steam stripping step would reduce X_t to zero, an economically unfeasible operation. Assuming equilibrium, the minimum benzene content of the washed gas, Y_o, will be mX_t. The optimum operating value of X_t can be determined only by an economic analysis defining the cost of removing each additional increment of light oil.

In order to secure the conditions that would lead to maximum absorption with the theoretical minimum oil-to-gas ratio very large equipment would be needed to provide the necessarily long contact times. It is common to use equipment of a reasonable size and to operate with an oil-to-gas ratio somewhat higher than the critical minimum value. Ratios of 12 to 15 gallons of wash oil per 1,000 cubic feet of gas are common at temperatures of 20 to 25° C. The desired excess can be easily determined if the scrubbing effectiveness of the particular towers employed has been evaluated in terms of the familiar concepts of "theoretical plates" or "transfer units." Souders and Brown, and Coret, have de-

rived an elegant expression [72] relating the scrubbing efficiency E to the oil-to-gas ratio and the effectiveness of the equipment as measured in theoretical plates (N):

$$E = \frac{Y_t - Y_o}{Y_t - mX_t} = \frac{\dfrac{L}{mG}\left[\left(\dfrac{L}{mG}\right)^N - 1\right]}{\left(\dfrac{L}{mG}\right)^{N+1} - 1}$$

It is again seen, for the general case, that the effectiveness of recovery for any one constituent is independent of the actual concentration in the gas. At the minimum oil-to-gas ratio, L/mG is equal to unity and the numerical value for any particular case can be considered to define the number of critical volumes of wash oil employed. The tabulation of the function in Table VII shows that any desired scrubbing efficiency can be obtained in many ways by employing various combinations of the oil-to-gas ratio and the number of theoretical plates. A design involving six to seven plates and the use of 1.5 to 2.0 critical volumes of oil will be found necessary in practice for economically complete recovery. Extrapolation from laboratory-scale absorption towers to plant-scale equipment is very unreliable, and it is usually necessary to evaluate any new departure in tower packing materials by a study of performance at a field installation. It is very roughly true in towers more than 4 feet in diameter that a theoretical plate or a transfer unit will be represented by 20 to 25 vertical feet of wooden hurdles and about 10 feet of steel turnings in present-day designs of scrubbing towers and under the usual conditions encountered. Superficial gas velocities of 1.8 to 3.5 feet per second are often employed.

[72] Souders, M., and Brown, G. G., *Ind. Eng. Chem.*, **24**, 519–22 (1932). Coret, G., *J. usines gaz*, **56**, 241–52 (1932).

· TABLE VII

$$\text{Value of } \frac{\dfrac{L}{mG}\left[\left(\dfrac{L}{mG}\right)^{N} - 1\right]}{\left(\dfrac{L}{mG}\right)^{N+1} - 1} \text{ for Various Values of } \left(\frac{L}{mG}\right) \text{ and } N$$

$\dfrac{L}{mG}$	$N=1$	2	3	4	5	6	7	8	9	10	∞
0.5	0.333					0.495					0.500
0.6			0.540				0.595				0.600
0.7			0.610				0.685				0.700
0.8			0.665				0.750				0.800
0.9			0.710				0.820				0.900
1.0	0.500	0.660	0.750	0.800	0.830	0.850	0.875	0.888	0.900	0.910	1.000
1.1			0.790				0.910				1.000
1.2	0.530	0.720	0.820	0.860	0.895	0.920	0.940	0.950	0.965	0.975	1.000
1.3			0.840				0.960				1.000
1.4			0.860				0.970				1.000
1.5	0.600	0.780	0.880	0.930	0.943	0.960	0.980	0.986	0.991	0.994	1.000
1.6			0.890				0.985				1.000
1.7			0.900				0.990				1.000
1.8			0.910				0.993				1.000
1.9			0.920				0.995				1.000
2.0	0.660	0.850	0.930	0.960	0.980	0.990	0.996	0.998	0.999	0.999	1.000

For purposes of simplification in the above, the terms "theoretical plate" and "transfer unit" have been used more or less interchangeably. It should be realized that the two are equal only if the operating and equilibrium lines are parallel, although no great error is introduced if the divergence is small. The lines are substantially parallel in the normal case, that is, temperatures of 20 to 25° C, an oil-to-gas ratio of 12 to 15 gallons per 1,000 cubic feet, and a light-oil content, in the debenzolized oil, of 0.3 to 0.4 percent. Under conditions considerably different from the normal the transfer unit should be used.

This concept has been utilized in making the calculations that are graphically set forth as Figs. 3 to 10. In these the per-cent recovery of the three major constituents of light oil has been set down as a function, in turn, of wash-oil rates, benzol-scrubber efficiencies, and wash-oil temperatures. The conditions chosen, more or less typical, are as follows:

	GALLONS PER TON COAL	VOLUME PERCENT
TOTAL LIGHT OIL IN GAS		
Benzol	2.21	67
Toluol	0.53	16
Xylenes	0.33	10
Solvents to 200° C	0.23	7
Total	3.30	100

Gas Yield per Ton of Coal: 11,000 cubic feet at 30 inches of mercury and 60° F; specific gravity 0.35.

Total Pressure in Benzol Scrubber: 800 milli-meters of mercury absolute.

Wash Oil:
  Specific gravity   = 0.88 at 20° C.
  Molecular weight = 260.

Debenzolized Wash Oil—Debenzolization: 0.35 percent by volume.

	VOLUME PERCENT
Benzene	0.00
Toluene	0.00
Xylenes	0.10
Solvents to 200° C	0.25
	———
Total	0.35

The absorption capacity of equipment for scrubbing light oil can, of course, be evaluated in terms of the well-known two-film absorption theory. It is very probable that the resistance of the wash-oil film is negligible and that the resistance of the gas film is controlling. Hence the rate equation can be written

$$GdY = M_A \alpha K_G a(Y - Y_e)dh$$

where M_A is the molecular weight of the light-oil constituent, $K_G a$ is the overall transfer coefficient, h is the height of the tower, $Y - Y_e$ is the potential across the film, and α is a constant introduced to convert the potential expressed in stoichiometric units into terms of partial pressure. Because of the linear relationship between Y and X the integration is simple and gives [69]

$$G(Y_i - Y_o) = M_A \alpha K_G a h(Y - Y_e)_{AV}$$
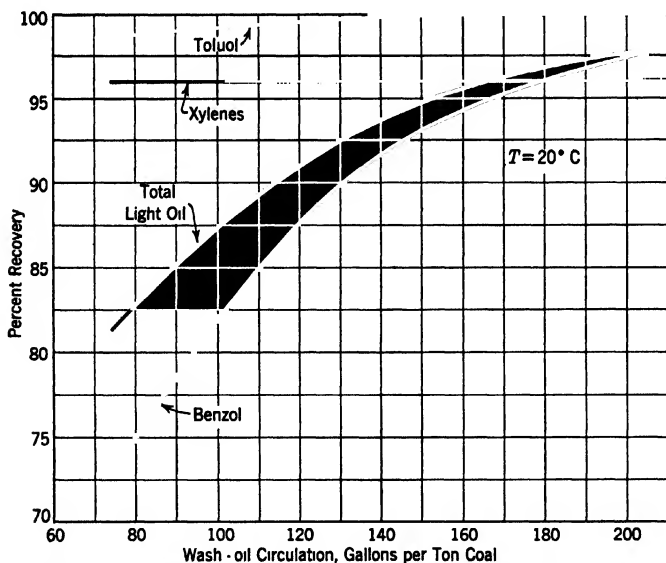
FIG. 3. Variation of recovery of the components of light oil with wash-oil circulation at 20° C.
  a. Scrubber equivalent to four transfer units.
  b. Molecular weight of wash oil, 260; specific gravity, 0 88
  c. 11,000 cubic feet of coke-oven gas (sp. gr. = 0.35) per ton of coal.
  d. Total light oil in gas, 3.30 gallons per ton of coal.
  e. Pressure in scrubber, 800 mm Hg absolute.
  f. Debenzolization of wash oil, 0.35 percent by volume.
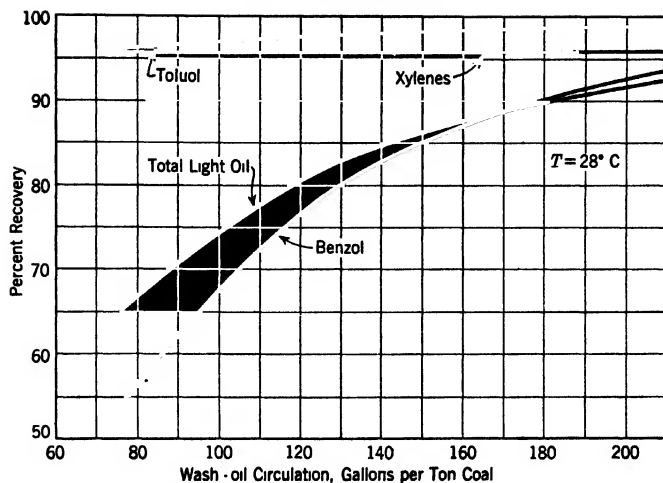
FIG. 4   Variation of recovery of the components of light oil with wash-oil circulation at 28° C. (Conditions as in Fig. 3.)
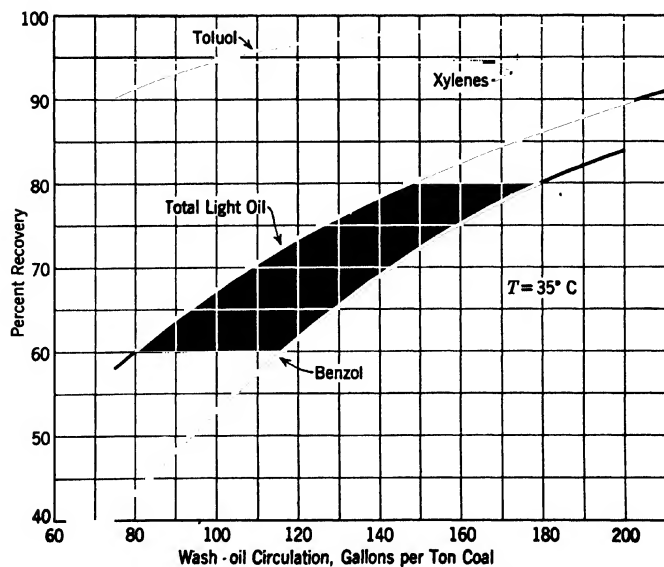
FIG. 5.   Variation of recovery of components of light oil with wash-oil circulation at 35° C.   (Conditions as in Fig. 3.)

where $(Y - Y_e)_{AV}$ is the familiar logarithmic mean between the terminal potential differences. For design purposes only $K_G a$ need be known; unfortunately published data are very meager. According to Sherwood,[69] several tests on large scrubbers gave an average $K_G a$ of 0.6 lb mol/(hr)-

perature of the vapor pressure of the key constituent of the light oil. Low absorption temperatures are necessarily desirable. At too low temperatures, the increased viscosity of the oil may result in poor distribution through the packing, and further reduction in temperature is hence often not
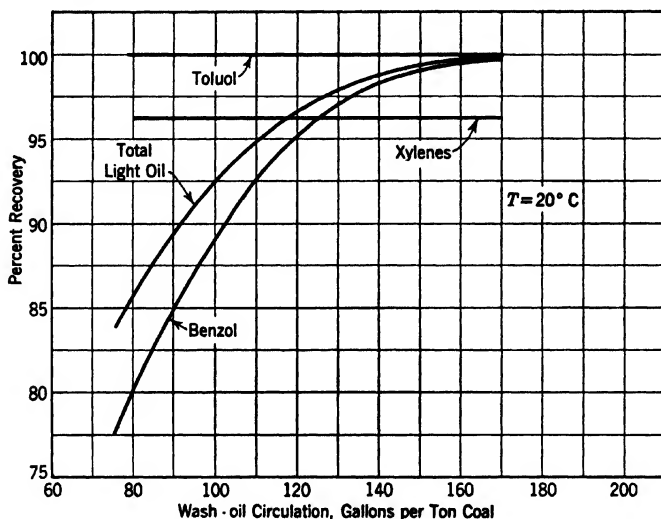
FIG. 6. Variation of recovery of the components of light oil with wash-oil circulation at 20° C. (Scrubber equivalent to six transfer units; other conditions as in Fig. 3.)

(cu ft) (atm) when operating at a gas rate of 240 lb/(hr)(sq ft) and an oil rate of 680 lb/(hr)(sq ft). The tower was 15 feet 6 inches in diameter and 111 feet tall, and it was packed with 7 inch by ¼ inch wooden slats spaced ½ inch apart on edge. Data for the variation of $K_G a$ with gas and oil rates, with the type of wash oil, with the type of packing, and with temperature are not available. The effect of temperature may be approximated from theoretical considerations. At any stated scrubbing efficiency the wash-oil rate must be varied with temperature in a manner directly proportional to the variation with tem-

useful. Wash-oil temperatures of 15 to 25° C are common.

A certain degree of selectivity for particular components can be secured by proper attention to the effectiveness of debenzolization and the magnitude of oil-to-gas ratio. Substantially complete removal of the toluene fraction coincidental with only partial removal of the benzene and xylene can be achieved by a combination of low oil-to-gas ratio and controlled steam stripping of the benzolized oil. Total selectivity may be obtained by a combination of: (a) complete recovery, (b) continuous separation of the crude light oil to

separate out the desired constituents, (c) continuous return of the unwanted fractions to the debenzolized oil entering the top of the scrubbing column.

Total scrubbing usually refers to washing and debenzolization conditions sufficiently thorough to remove all the benzene and consequently all the higher-boiling con-

more properly be classified as gas purification processes.

When substantially complete light-oil recovery is desired the packed tower operating with countercurrent flows is the only economically practical type of system. Any deviation from the strictly countercurrent mode of operation leads to ineffi-
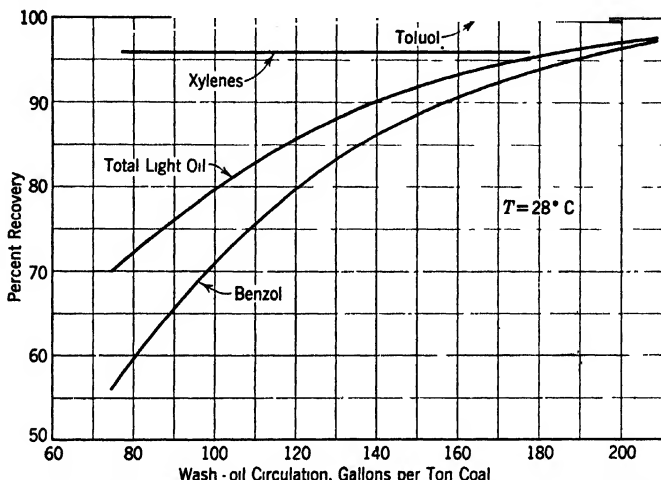
Fig. 7. Variation of recovery of the components of light oil with wash-oil circulation at 28° C. (Conditions as in Fig. 6.)

stituents of light oil. The choice of benzene as the key constituent is arbitrary, and light-oil-recovery plants may be designed for total recovery of other components. By suitable operation recovery may be restricted to naphthalene and gum formers,[71] or, proceeding to the other extreme, complete removal of the carbon disulfide may be practiced. In an English installation substantially complete recovery of the carbon disulfide could be attained by wash oil-to-gas ratios of 31 gallons of wash oil per 1,000 cubic feet of gas.[73] These extreme applications of light-oil recovery can

ciency and increased operating costs. Nevertheless, there has been a limited application, particularly at gas plants and in foreign practice, of a wide variety of ingenious static and nonstatic multistage washers. In general, the gas is treated with wash oil in a number of successive bays in each of which the oil is circulated or mixed. Contact may be brought about by bubbling the gas through the oil, by spraying the oil through the gas path, or by passing the gas over surfaces wetted with the liquid. The flow from bay to bay may or may not be countercurrent. In any event the efficiency of extraction is less than that of a properly designed tower

73 Cooper, C., *Gas World,* 108, No. 2796, Coking Sect., 27–31 (1938).

scrubber, and the desirability of employing such devices has never been very clear   A mathematical analysis of multistage scrubbers has been made by Silver [74]

Since extrapolation from small-scale laboratory gas washing towers to large-scale a few notable exceptions, has been on an empirical, completely rule-of-thumb basis It is beyond the scope of this discussion to do more than call attention to the fact that both the theoretical and analytical tools are available and that they could very
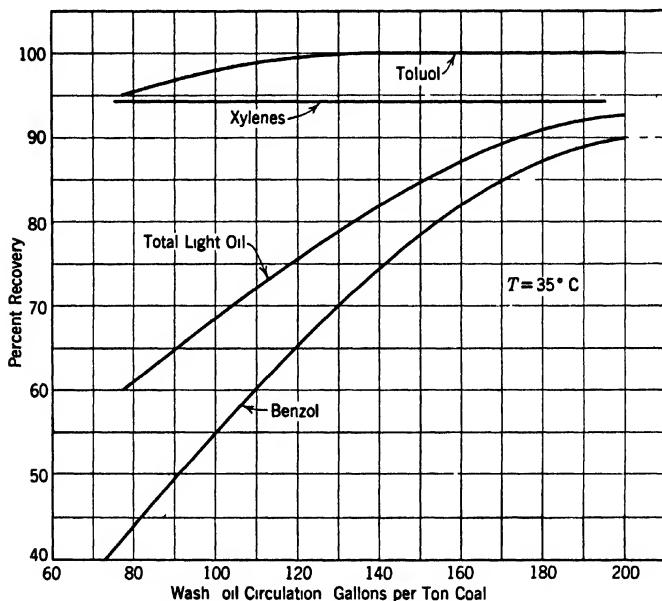
Fɪɢ 8   Variation in recovery of the components of light oil with wash oil circulation at 35° C (Conditions as in Fig 6)

equipment is associated with many pitfalls, the proper design of light-oil scrubbers must be based on fundamental transfer data obtained in tests made on existent installations   Although the theoretical knowledge necessary to evaluate any such experimental study has long been available, there has been apparently considerable reluctance on the part of designers of light-oil plants to carry out the requisite systematic studies   Scrubber design, with

profitably be applied to the technology of light-oil recovery

The literature on gas washing and absorbing column design is exhaustive   For an amplification of the oversimplified exposition that has been given here the reader is referred to a selected list of papers on gas washing and absorber design [75]

74 Silver, L, *Trans Inst Chem Engrs (London)* 12, 64–85 (1934).

75 Lewis W K , *Ind Eng Chem* , 8, 825–33 (1916)   *Trans Am Inst Chem Engrs* , 20, 1–7 (1927)   Whitman W G and Keats I L *Ind Eng Chem* , 14, 186–91 (1922)   Lewis, W K , and Whitman W G *ibid* , 16, 1215–20 (1924) Cantelo, R C , *Chem & Met Eng* , 33, 680–1
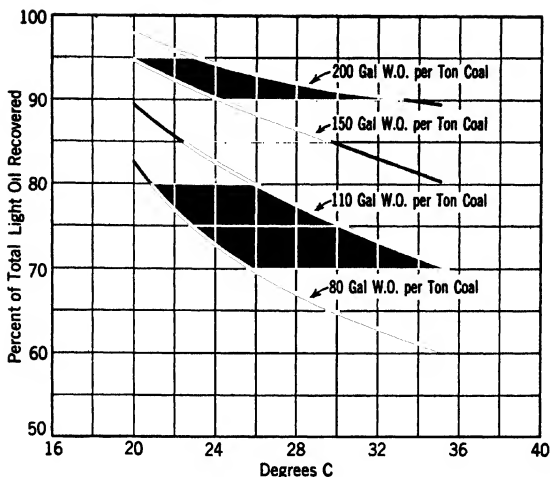
Fɪɢ. 9. Variation of recovery of light oil with wash-oil temperature. Scrubber equivalent to four transfer units.

The Washing Menstruum. The economics of light-oil recovery by the liquid-absorbent process depends, to a great extent, upon the particular properties of the wash oil employed. It is simple to design a plant efficiently adaptable to all possible types of coal gas; it is relatively more difficult to devise equipment operable with all types of wash oils. Details of design and meth-

(1926). Lewis, W. K., and McAdams, W. H., *Ind. Eng. Chem.*, **20**, 253–7 (1928). Rosebaugh, T., *Chem. & Met. Eng.*, **35**, 144–8 (1928). Murray, I. L., *Ind. Eng. Chem.*, **22**, 165–7 (1930). Simmons, C. W., and Long, J. D., *ibid.*, **22**, 718–21 (1930). Bolzinger, A., *J. usines gaz*, **56**, 356–7 (1932). Wearing, C. M., *Gas J.*, **201**, 750–4, 814–8 (1933); *Gas World*, **98**, 276–9, 311–6 (1933). Hollings, H., and Silver, L., *Trans. Inst. Chem. Engrs.* (*London*), **12**, 49–63 (1934). Chilton, T. H., and Colburn, A. P., *Ind. Eng. Chem.*, **27**, 255–60 (1935). Hixson, A. W., and Scott, C. E., *ibid.*, **27**, 307–14 (1935). Siron, A., *J. usines gaz*, **59**, 231–42 (1935). Rosendahl, F., *Chem. App.*, **25**, 193–211 (1938). Baker, E. M., and Wiegand, J. H., *Trans. Am. Inst. Chem. Engrs.*, **35**, 237–54 (1939). Dolch, P., *Feuerungstech.*, **27**, 161–73 (1939). White, G. E., *Trans. Am. Inst. Chem. Engrs.*, **36**, 359–69 (1940).

ods of operation are less dependent upon the composition of the recovered product than upon the nature of the recovery medium. The defining influence of the wash oil may be strongly felt in the purification process and may even determine, in part, modes of ultimate utilization of the scrubbed coke-oven gas.

The desirable properties of a liquid absorbent can be set forth in the description of a hypothetical ideal wash oil:

1. The absorptive capacity of the oil should be very high; that is, the constant m in the Henry's law relation $Y = mX$ should be as small as possible. The oil-to-gas ratio is a direct function of m; when m is small, the volume of oil upon which expensive pumping, heating, cooling, and regenerating operations must be carried out is also correspondingly small.

2. The specific heat of the oil should be small since, in the stripping operation, the recovery of each gallon of light oil involves

the heating to about 120° C or higher of many volumes of wash oil.

3. The vapor pressure of the wash oil at the average temperature of the scrubbing operation should be small to prevent undue loss, by vaporization, of the oil to the gas.

finic content of benzols, toluols, and xylols cannot be traced to the use of petroleum wash oils but can be more readily correlated with carbonization conditions.[76]

5. The viscosity of the oil should be as low as possible and should increase only slowly with a decrease in temperature. A
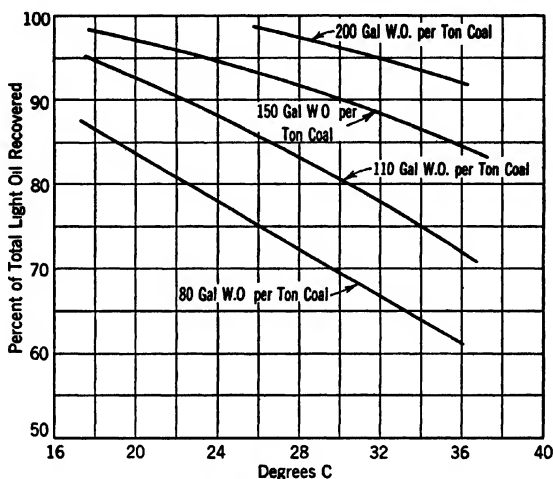
Fig. 10   Variation of recovery of light oil with wash-oil temperature   Scrubber equivalent to six transfer units.

4. The initial boiling point of the oil should be as high as possible; that is, it should contain no appreciable quantity of low-boiling material   The ease with which the subsequent separation of benzolized oil into light oil and wash oil can be carried out is chiefly a function of the difference between the boiling points of the two materials.   If this difference becomes too small the higher-boiling products of the light oil may become contaminated with the most volatile portion of the wash oil.   In petroleum wash oils the overall result may be the introduction of "paraffins" into the heavy solvent fraction of the light oil.   Comparative tests with creosote oils and petroleum oils have shown that the paraf-

low viscosity favorably affects the distribution of the washing medium over the packing surface and thereby tends to increase the coefficients of mass and heat transfer through the liquid film [77]

6. The specific gravity of the wash oil should be as far removed from that of water as possible.   "Whether this is really necessary, and the actual range of specific gravity to be avoided, would appear to be a matter of opinion   With care in plant operation, actual admixture of wash oil with water is avoidable.   Moreover, the

[76] The National Benzole Association, *Seventh Rept. Joint Benzole Research Com*, **1930**, 121.
[77] The National Benzole Association, *Fifth Rept. Joint Benzole Research Com.*, **1928**, 100.

danger of emulsification of the oil by water undoubtedly varies with the type of oil used; e.g., oils containing phenols are more liable to emulsification with water than purely hydrocarbon oils. For the reasons given, however, a specific gravity higher than 1.02 or lower than 0.98 may be ·regarded as desirable.[11, 77]

7. The oil should maintain its initial properties under working conditions for as long a period as possible. Particularly the oil should not thicken, increase in molecular weight, or combine with any of the impurities in the gas to form resins or insoluble sludges.

8. The oil should not contaminate the gas with any undesirable compounds. A tar oil high in naphthalene would, for instance, be quite unsuitable for use at a gas plant where restrictions are placed on the naphthalene content of the send-out gas.

9. The oil should be cheap and indigenous to the country of use.

Although a very large number of materials have been described and recommended as suitable absorbents, only a few have found extensive commercial utilization. Usually either a petroleum oil or tar oil is used. In German practice coal-tar oils and brown-coal tar oils have been utilized almost exclusively; in England, since 1923, when the first economically significant utilization of petroleum wash oils occurred, petroleum oils have largely supplanted coal-tar oils; in the United States petroleum oils are at present invariably employed. The miscellaneous materials, some of only historical interest, include: tetralin, nitrobenzene, aniline, green oil, cresol, shale oil, low-temperature tar oils, Bergius-tar oils, blast-furnace creosotes, tar, and naphthalene (additive in solution).

PETROLEUM OILS. "Gas oils," "straw oils," and "spindle oils" are so inexpensive compared with the various creosote oils that this factor alone easily outweighs the disadvantage of these materials in domestic applications. The chief objections to petroleum wash oils are: (a) the formation of sludge which precipitates on heating surfaces, and (b) the relatively low absorbent capacity of the material.

A typical, currently available oil may be described by abstracting the specifications of a large user of wash oil: (1) *specific gravity*—the specific gravity shall be determined by means of a hydrometer or Westphal balance and must not be over 0.875 at 15.5° C/15.5° C; (2) *viscosity*—the viscosity must not be more than 69 Saybolt seconds at 38° C and not greater than 150 seconds at 4° C; (3) *emulsification*—when 100 milliliters of the oil is shaken vigorously for 20 minutes with 100 milliliters of distilled water in a 250-milliliter glass-stoppered cylinder at 21° C at least 95 percent of the oil must separate in 10 minutes; (4) *boiling range*—not more than 1 percent of the oil shall distil under 300° C, and not less than 90 percent under 370° C; and (5) the residue of carbonaceous or other material from the oil shall not be more than 0.10 percent by weight when subjected to a temperature of 140 to 145° C for 120 hours.

As a further example, a specification of the U. S. Bureau of Standards for a straw oil suitable for light-oil recovery is as follows: (1) *specific gravity* (60° F/60° F), not less than 0.86; (2) *flash point,* not less than 135° C (open-cup tester); (3) *viscosity,* not more than 70 seconds at 37.7° C (100° F) by Saybolt viscosimeter; (4) when 500 milliliters of the oil is distilled with steam at atmospheric pressure, collecting 500 milliliters of condensed water, not more than 5 milliliters of oil shall have distilled over; (5) the oil remaining after the steam distillation shall be poured into a 500-milliliter cylinder and shall show no

permanent emulsion; and (6) the oil shall not lose more than 10 percent by volume on washing with 2.5 times its volume of 100 percent sulfuric acid, when vigorously shaken with the acid and allowed to stand for 2 hours.

Although not mentioned in the above specifications the paraffinic or naphthenic nature of the oil is believed to have some bearing on the value of the oil as a wash oil. Special distillates, almost wholly either naphthenic or paraffinic, are now available for use as recovery media.

It is very desirable that the specifications of an absorbent medium include a test that is a measure of the absorptive capacity,[78] as, for example, a determination of m in the relation $Y = mX$. Wilson and Davis, in an investigation of seven oils, disagreed with this view and claimed that no absorption test was necessary.[71] They found substantially identical capacities for all the oils tested; the absorptive capacity seemed to bear no relation to the molecular weight when the molecular weight was determined by a cryoscopic method. Unfortunately, the molecular weight of oil determined by any procedure involving dilute solution in a solvent quite often bears little relation to the effective molecular weight computed from vapor-pressure relationships. The olefin content of the oil seems to be of little importance; Mathias found the desirable specifications to include: specific gravity, viscosity, loss on steam distillation, emulsion test, initial boiling point, pour test, and oxidation sludge test.[79]

Although the absorptive capacity of fresh petroleum wash oils is considerably less than that of fresh creosotes,[71, 76] this advantage of tar oils rapidly disappears on use.[80] Tar oils tend to increase in viscosity and molecular weight owing to the solution of resinous substances; in petroleum oils the resinous materials are chiefly deposited as a sludge, and the residual oil, showing only a slight increase in viscosity and decrease in absorptive capacity, is still suitable for use.[81] The precipitated sludge tends to collect on heat-transfer surfaces and, unless removed, or its formation inhibited, leads to considerable difficulty. Although the mechanism of sludge formation is not well established it is generally agreed that the precipitate is a high-boiling component of coal tar relatively soluble in the benzolized oil but correspondingly insoluble in the debenzolized oil. Ullman[82] found that sludging was prevented by the prior treatment of the gas with an effective electrostatic precipitator. It seems generally established that petroleum wash-oil sludges are usually characterized by a high content of sulfur compounds. More recent work indicates that some of the sludge may be formed by the polymerization and perhaps reaction with some constituent of the wash oil of either styrene, indene, or coumarone.[83]

A large variety of methods have been used either to prevent the formation of sludge or to remove mechanically the already formed precipitate from the oil. Karrer and Lusby,[83, 84] in their procedure, added an anti-oxidant to the oil before introduction in the system. Practically, about 0.5 percent of a hardwood tar dis-

[78] König, E., *Glückauf*, **73**, 325–30 (1937).

[79] Mathias, H. R., *Ind. Eng. Chem.*, **23**, 804–7 (1931).

[80] Pannertz, F., *Gas- u. Wasserfach*, **65**, 113–5 (1922). Bunte, K., and Frei, E., *ibid.*, **65**, 273–7

(1922). Nübling, R., and Engler, *ibid.*, **67**, 551–2 (1924). Weindel, A., *Gas J.*, **173**, 92–4 (1926).

[81] White, F., and Kellett, S., *Gas World*, **96**, Coking Sect., 68–75 (1932).

[82] Ullman, H. M., Chamberlin, D. S., Simmons, C. W., and Thorpe, M. A., *Ind. Eng. Chem.*, **21**, 313–4 (1929).

[83] Lusby, O. W., and Utermohle, C. E., *American Gas Assoc., Joint Com. Conf. Production & Chem. Coms.*, New York, **1940**, May 20–22.

[84] Karrer, S., and Lusby, O. W., U. S. Pat. 2,191,486 (1940).

tillate has been found very effective even at elevated temperatures, a circumstance which makes possible the use of high temperatures with a concomitant small live steam demand in the debenzolization step. A clay filter of 60 to 90 mesh material was employed to remove the small amount of residual sludge that was formed despite the inhibiting action of the hardwood distillate; this filter material contributed to the effectiveness of the process.

A similar problem of reconditioning absorbent oils exists in the petroleum industry. Usually some application of fractional distillation has been employed, either at atmospheric pressure using a fire still, or under reduced pressures using indirect steam boiling coils. A rather large amount of specialized equipment is necessary.

Many of the disadvantages of former distillation methods of purification are avoided by a very simple scheme of Stover's,[85] which, in addition to use by the petroleum industry, has been enthusiastically adopted by the designers of modern light-oil-recovery plants.

The purification unit consists of a still— a tank with trays or baffles—and a heater, operating in conjunction with the debenzolizing still. No auxiliary equipment such as a condenser, a condensate receiver, or a pump is required. The agitation steam which normally enters the base of the debenzolizing or stripping still is diverted to pass through the purifier where it vaporizes the wash oil contained therein. This steam, saturated with oil vapors, then flows into the debenzolizing still and performs its stripping action in the normal manner. Raw oil from the plant system flows by gravity to the purifier, the amount of feed being automatically regulated by a liquid level controller. The raw oil stream is usually removed from one of the upper trays of the stripping still. Nonvolatile sludge gradually accumulates in the base of the purifier, whence it is drained at infrequent intervals to a muck tank. Oil is fed to the purifier as rapidly as it is evaporated, but the amount is usually small, averaging less than 1 percent of the total oil circulation. Theoretically, no additional steam is used in operating the process; practically, the amount of additional steam is negligible. A somewhat similar procedure has been described by Rector.[86] The Stover system has been combined with the inhibitor process of Karrer and Lusby in one installation.

A few other schemes for the regeneration of spent petroleum oils may be briefly mentioned. A portion of the foul oil may be periodically withdrawn and filtered in a filter press[87] or a portion may be continuously withdrawn and centrifuged.[88] Regeneration by washing with hot water has been recommended.[89] Since the sludge is more insoluble in low-boiling hydrocarbons the addition of these to precipitate the sludge followed by fractional distillation to remove the added component has been proposed.[90] Weindel has developed a continuous process suitable for both petroleum oils and tar oils. The spent absorbent is distilled in a fire still, the charge being agitated by a small current of debenzolized gas, which is returned to the suction gas

[85] *Refiner Natural Gasoline Mfr*, 18, No. 2, 89–90 (1939). Stover, W. A., U. S. Pat. 2,196,-878 (1940).

[86] Rector, N. K., U. S. Pat. 2,164,593 (1939).

[87] Otto, C., and Co. G.m.b.H., Ger. Pat. 502,189 (1930). Weller, W., *Gas- u. Wasserfach*, 80, 746–8 (1937).

[88] Minot, M., *Chimie & industrie*, 21, 252 (1929). Sharples, P. T., U. S. Pat. 1,766,196 (1930).

[89] Schönehorn, H., U. S. Pat. 1,980,009 (1934). Still, C., Brit. Pat. 460,478 (1937).

[90] Stinnes, Z. M., and Klemstedt, H., Ger. Pat. 408,030 (1925). Finn, C. P., Brit. Pat. 495,789 (1938).

main before the coolers.[91]   Jones treated
the spent oil at a temperature below 70° C
with 2 to 10 percent by volume of 60 to
66° Baumé sulfuric acid; the sludge formed
was removed and the oil washed with water
and dilute aqueous alkali solution.[92] Mos-
tart produced coagulation of the sludge

particles by the addition of suitable electro-
lytes.[93]

TAR OILS. On the Continent and in Eng-
land, creosote oil has been more widely
used than any other absorbent. Prepared
by the simple distillation of coke-oven tar,
the material is indigenous to any coke
plant. As reference to Table VIII [94] will

91 Thau, A., *Gas World*, **103**, Coking Sect.,
84–6 (1935).
92 Jones, I. H., U. S. Pat. 1,949,746 (1934).

93 Mostart, G., Brit. Pat. 499,354 (1939).
94 See pp. 218–9 of ref. 6.

TABLE VIII

PROPERTIES OF WASH OILS FOR BENZOLE RECOVERY [94]

Wash Oil (fresh)	Distillation Range	Sp. Gr. (20°/20° C)	Viscosity 20° C	Volatility (loss to gas) at 20° C		Absorptive Capacity Concentration of Benzene in Liquid in Equilibrium with Benzene Vapor at 6.5 mm Pressure	
	temperatures in °C	(1.05)	Redwood seconds	grams per cubic meter	gallons per million cubic feet	grams per 100 grams solution	volumes per 100 volumes absorbent
1. Naphthalene (in solution)	(b.p. 218)	(1.05)	....	....	....	5.5	....
2. (a) Tetralin	205°–207°	0.976	30.5	1.9	12.2	5.25	6.15
(b) Tetralin (commercial)	206°–225°	0.975	30.5	1.8	11.7	4.9	5.7
(c) Tetralin (b) + 10% by wt. of naphthalene	206°–225°	0.9825	31.0	1.9	11.75	4.95	5.85
3. Nitrobenzene	211°–212°	1.206	28.5	1.5	7.75	3.6	5.15
4. Creosote, light fraction (free from tar acids)	205°–265°	0.9535	30.5	2.8	18.3	4.55	5.15
light (chlorinated)	200°–95% at 288°	0.976	31.0	2.15	13.7	4.3	5.0
sulfur-treated (refractionated, tar acids 6% by vol.)	220°–95% at 320°	0.9875	36.5	1.8	11.4	4.1	4.8
light (tar acids 17.5% by vol.)	200°–95% at 300°	1.0135	34.5	1.9	11.7	3.95	4.75
medium (tar acids 20% by vol.)	200°–90% at 350°	1.031	37.5	2.0	12.1	3.6	4.35
blast-furnace (washed)	210°–95% at 340°	0.935	40.0	1.0	6.7	3.65	4.05
5. Aniline	184°–185°	1.0235	36.0	2.2	13.4	3.4	4.1
6. Green oil	250°–90% at 385°	1.088	70.0	0.45	2.7	2.95	3.75
7. Cresol (mixed isomers)	197°–206°	1.039	65.0	0.77	4.6	2.8	3.4
8. Shale oil	226°–95% at 390°	0.838	38.0	0.60	4.5	3.05	3.0
9. Gas oil—light fraction	214°–95% at 285°	0.8295	32.5	1.7	13.0	3.2	3.1
(a)	210°–95% at 400°	0.8635	40.0	1.75	12.5	2.9	2.95
(b)	260°–95% at 365°	0.849	44.5	0.9	6.7	2.8	2.8
(a) + 12% by wt. of naphthalene	210°–95% at 400°	0.8805	37.0	. .	....	3.3	3.4
10. Low-temperature-tar fraction, (a) containing phenols (39% by vol.)	200°–95% at 345°	0.981	52.5	2.05	12.9	3.35	3.87
(a) free from phenols	220°–95% at 357°	0.962	41.5	1.0	6.7	3.75	4.27
(b) containing phenols (41% by vol.)	206°–95% at 321°	0.984	51.5	1.2	7.5	3.55	4.12
(b) free from phenols	200°–95% at 320°	0.935	34.5	2.9	19.2	3.95	4.37
11. Bergius-tar fraction, containing phenols	200°–95% at 340°	0.986	44.0	1.2	7.5	3.75	4.37
free from phenols	200°–95% at 305°	0.946	32.0	3.3	21.6	4.2	4.7

show, the absorption capacity is considerably higher than that of typical petroleum oils. Unfortunately this high absorptive capacity is not long maintained since creosotes tend to thicken very markedly on use, necessitating the installation of somewhat elaborate regeneration plants. Because of their comparatively high price,

creosote oils are, without exception, not used as light-oil absorbents in the United States. Occasionally, depending upon the mode of preparation, they may be unsuitable for use at gas plants where a send-out gas free from naphthalene is required. The following are two typical British specifications:

SPECIFICATION OF THE DEPARTMENT OF EXPLOSIVES SUPPLY [95]

Specific gravity at 60° F	1.010 to 1.030
Tar acids	Immaterial (usually 8 to 9 percent)
Naphthalene	Should deposit none on cooling to 55° F
Initial boiling point	Should not boil below 200° C
Distillation range	Not less than 70 percent or more than 90 percent at 300° C

WALMSLEY AND MORFEY'S SPECIFICATION [95, 96]

Specific gravity	1.035
Drip point	210 to 220° C
50 percent distillate at	250° C
80 percent distillate at	300° C
Water	Traces
Naphthalene	Distillate to 300° C should not settle out more than 7 percent of solids at 45° F

Typical German specifications may be given as follows: [97]

DESCRIPTION	DISTILLATION RANGE	NAPHTHALENE CONTENT	WATER CONTENT
Benzole absorbing-oil "80 percent"	Max. 10 percent at 200° C Min. 80 percent at 300° C	Max. 10 percent	Max. 1 percent
Benzole absorbing-oil "90 percent"	Max. 10 percent at 200° C Min. 90 percent at 300° C	Max. 10 percent	Max. 1 percent
Solvay oil	Max. 1 percent at 210° C Min. 90 percent at 300° C Distilling as evenly as possible 210 to 300° C	No precipitate after ¼ hour at 0° C	Max. 1 percent

Coal-tar wash oils are usually prepared by segregation of the appropriate fraction during the simple distillation of coal tars, with treatment to remove crystallizable substances, phenols, and pyridines.[98] Other

procedures, including the fractional condensation of the tar from the hot coke-oven gas, have been described.[99]

The absorptive capacity of creosote wash oils has been rather thoroughly investigated by Nübling [80] and others.[100] The absorp-

95 Whitehead, S. E., *Benzol,* Van Nostrand & Co., New York, 1920, p. 46.

96 Warnes, A. R., *Coal Tar Distillation,* Van Nostrand & Co., New York, 3rd ed., 1923, pp. 344, 361.

97 Jenkner, A., *Coal Carbonization,* 2, 70 (1936).

98 Frey, K., *Brennstoff-Chem.,* 14, 241-5 (1933).

99 Gruhlke, H., *Gas- u. Wasserfach,* 67, 362-3 (1924). Nicklin, M. E., Brit. Pat. 230,681 (1925). Tschebotarev, P. M., *Coke and Chem.* (*U.S.S.R.*), 6, 46-99 (1935).

100 The National Benzole Association, *Repts. Joint Benzole Research Com.,* 1926, pp. 133-4; 1928, pp. 117-36. Brückner, H., and Gruber, H.,

tive capacity, generally speaking, is a function of both the distillation range and the detailed chemical composition of the tar oil. Lowering the average boiling point decreases the average molecular weight and thereby produces an increase in absorptive capacity. Frequently, however, a favorable alteration in boiling range is accompanied by a detrimental variation in the ratio of the various components. The influence of tar acids and naphthalene is especially notable. Tar acids in low concentrations are presumably unassociated; in appreciable concentrations considerable association seems to exist.[101] As a result, the presence of either low- or high-boiling tar acids is definitely undesirable.[78] The dephenolization of wash oils by countercurrent treatment with alkali in a packed column has been described.[102] The cost of completely removing phenols from creosotes is usually sufficiently high to negate any economies due to the resultant increased absorptive capacity. With respect to naphthalene, Hoffert and Claxton[103] found that: (1) naphthalene in solution in most wash oils behaves normally and has an absorptive capacity of 5.5; (2) the addition of naphthalene to an oil of low absorptive capacity causes an appreciable increase in the absorptive capacity; (3) the effect of the addition of naphthalene becomes less, the nearer the absorptive capacity of the oil approaches 5.5; and (4) if the absorptive capacity and the naphthalene content of an oil are known, it is possible to calculate, approximately, the

absorptive capacity of the oil with any other naphthalene content.

The addition of naphthalene to a coaltar wash oil will, in general, increase the density and decrease the viscosity. Mechanical difficulties are experienced in the separation of water,[104] and the use of high-naphthalene wash oils usually entails special plant design.[97, 105]

Unquestionably the most important phenomenon associated with the use of creosotes as light-oil absorbents is the great increase in viscosity that occurs during use, necessitating frequent regeneration. Unlike gas oils, little mechanical difficulty is experienced through the deposition of insoluble sludges. The mechanism of the thickening process is not definitely established, and many differences of opinion exist. Hoffert and Claxton[106] have summarized the suggestions of various investigators:

1. Removal of the lower-boiling constituents in the debenzolizing still.[107]
2. Accumulation of solid and resinous material from the tar fog that passes through to the benzole scrubbers.[108, 109, 110]
3. Interaction of impurities in the gas with constituents of the oil to give polymerized high-boiling compounds: (a) action of oxygen on certain constituents of the oil, particularly phenols;[111, 112, 113, 114, 115, 116] (b) action of

Gas- u. Wasserfach, **77**, 897–901 (1934). Koeppel, C., *ibid.*, **83**, 73–9 (1940). Müller, F., Freude, F., and Kaunert, P., *ibid.*, **83**, 521–7 (1940).

101 Hewitt, J. T., and Winmill, T. F., *J. Chem. Soc.*, **91**, 441–8 (1907). Philip, J. C., and Clark, C. H. D., *ibid.*, **127**, 1274–7 (1925).

102 Mezger, R., *Glückauf*, **61**, 122 (1925).

103 The National Benzole Association, *Rept. Joint Benzole Research Com.*, **1928**, 151, 163.

104 Goldschmidt, F., *Gas- u. Wasserfach*, **73**, 636–7 (1930).

105 Still, C., Brit. Pats. 293,702, 300,964 (1927).

106 See p. 253 of ref. 6.

107 R. A. R., *Gas World*, **95**, Coking Sect., 116–17 (1931).

108 Thau, A., *Gas- u. Wasserfach*, **67**, 163–5 (1924).

109 Nesterov, N. P., *Coke and Chem.* (*U.S.S.R.*), **1936**, 46–50.

110 Gerhard, *Gas- u. Wasserfach*, **66**, 189–91 (1923). Stumpf, K., *ibid.*, **67**, 515–8 (1924).

111 Schulte, F., *Glückauf*, **71**, 653–7 (1935).

112 Bordo, J. A., and Mühlendyck, W., *Brennstoff-Chem.*, **14**, 107–12 (1933).

113 Bardagov, I. T., and Dal, V. I., *Chimie & industrie*, **40**, 1081 (1938).

114 Kiemstedt, H., *Brennstoff-Chem.*, **6**, 185–8, 201–5 (1925).

hydrogen sulfide and of sulfur on the unsaturated constituents of the oil; [111, 113, 115, 116, 117] (c) action of sulfuric and sulfonic acids (formed by the oxidation of hydrogen sulfide), on the unsaturated constituents of the oil; [109, 118] (d) NH_3, NO, HCl, HCN, C_2N_2, and CO_2 may be added to the above tabulation.[109, 112, 114]

4. Cracking and polymerization.

The resinous substances, whatever their source, are characterized by almost complete solubility in the wash oil. The most satisfactory methods of regenerating spent creosotes involve some type of distillation. Discontinuously, the wash oil in the system may be completely replaced with fresh material, the spent absorbent being worked up in batch stills. More economic is the continuous withdrawal of 2 to 4 percent of the hot debenzolized oil, the purification being carried out by a continuous distillation in small gas-fired equipment.[119] Two stills are generally used; in some applications regeneration is combined with the manufacture of wash oil.[120] Hydrogen sulfide is usually liberated during regeneration and may form a fire hazard through the formation of ferrous sulfide; it has been proposed to add, before regeneration, substances which split off sulfur dioxide, for example, the resinous oils derived from the regeneration of acid sludges of light-oil washing.[121]

Among other schemes of regeneration may be mentioned mild cracking in the presence of a cracking catalyst,[122] hydrogenation of a continuously withdrawn portion,[123] washing with hot water,[124] vacuum distillation,[91] and the addition of heavy boiling phenols.[125]

MISCELLANEOUS TAR OILS. Suitable wash oils can be prepared by distillation of lignite tars, and such materials have found considerable use in Germany. Lignite tar oils are paraffinoid and possess properties approximating those of petroleum wash oils, for example, freedom from naphthalene and a tendency to precipitate resinous sludge.[126] As would be expected, lignite tar oils have a lower absorptive capacity for light oils and naphthalene.[118, 127] They have been successfully used in the recovery of low-temperature light oils.[128] The molecular weight of an oil distilling 10 percent at 260° C, 90 percent at 340° C, will be not far from 200.

Low-temperature tar oils have been suggested as absorbents for coke-oven light oil.[129] Hoffert and Claxton found that the absorptive capacities of the low-temperature tar distillates and Bergius-tar distillate were approximately the same as those of the corresponding distillates, with and without removal of phenols, obtained from high-temperature tars (creosotes) of similar distillation range. Low-temperature tar oils were somewhat less stable during use

115 Winter, H., and Free, G., *Gluckauf*, **70**, 1028–31 (1934).

116 Demann, W., and Brösse, W., *Tech. Mitt. Krupp*, **4**, 9–16 (1936).

117 Offe, G., *Gas u Wasserfach*, **66**, 394-6 (1923), **67**, 67–9 (1924), **68**, 136 7 (1925).

118 Kattwinkel, R., *ibid.*, **67**, 474–5 (1924), **68**, 323–4 (1925).

119 Holmes, W. C., & Co. Ltd., Brit Pat. 393,-041 (1933). Clayton Son & Co., Ltd., Brit. Pat. 419,545 (1934). Green, W., *Gas World*, **107**, Coking Sect., 96–9 (1937).

120 Larke, R. H., *Gas World*, **112**, 132–4 (1940).

121 Schmidt, H., Ger. Pat. 524,562 (1931).

122 Concordia-Bergbau A.-G., Ger. Pat. 677,019 (1939).

123 Vereinigte Stahlwerke A.-G., Ger. Pat. 624,-321 (1936).

124 Still, C., Ger Pat. 622,370 (1935).

125 Kohle- und Eisenforschung G.m.b.H., Ger. Pat. 640,340 (1936).

126 See Nübling and Engler in ref. 80. Jacobsohn, F., *Teer u. Bitumen*, **27**, 617–20 (1929).

127 See Stumpf in ref. 110. Thau, A., *Glückauf*, **61**, 117–26 (1925). Trutnovsky, H., *Teer u. Bitumen*, **27**, 477–80 (1929).

128 Müller, F., *Gas- u. Wasserfach*, **68**, 393 (1925).

129 I. G. Farbenindustrie A.-G., U. S. Pat. 1,818,158 (1931).

than the corresponding high-temperature oils.[130]

Although never available in large quantities, blast-furnace creosotes have found use as light-oil absorbents. The absorptive capacity of a washed blast-furnace creosote is about the same as that of a coal-tar creosote of similar distillation range and tar acid and naphthalene content.[131] Blast-furnace creosotes are characterized by proportionately high viscosities compared with ordinary tar-oil absorbents. Whittaker[132] discussed the preparation and use of this material.

Among tar oils may be included "green oil" or strained anthracene oil. This absorbent is prepared by chilling heavy oil and removing the crude anthracene. It was used during World War I;[133] its subsequent use by some operators is based upon considerations of its high distillation range (and hence low volatility), high specific gravity, and freedom from naphthalene. Among disadvantages are a low absorptive capacity and the possibility of anthracene blockages, which are extremely difficult to remove because of the high melting point of the principal constituents.[134]

MISCELLANEOUS WASH OILS. During World War I, it was discovered that cresol was an excellent absorbent for alcohol and ether vapors, and this utilization was patented by Daniel and Brégeat.[135] Claims were soon set forth[136, 137] for light-oil re-covery using this absorbent medium; a large-scale application was made in 1924 at the Northampton works of the Bethlehem Steel Corporation but, significantly, was operated for only a short time.[138] Subsequent work has shown that although cresol has a high absorptive capacity for oxygen-containing compounds such as alcohol, ether, and acetone its behavior with aromatic hydrocarbons is quite different and compares somewhat unfavorably with gas oils and creosotes.[78, 139] Cresol and cresols possess many disadvantages as light-oil absorbents, particularly their high cost, ease of resinification, high viscosities and specific heats, relatively high solubility in water, and high volatility. The last factor makes necessary some procedure to recover cresol vapors from the debenzolized gas.[136, 140]

The suggestion that tetralin, tetrahydro-naphthalene, be used as a light-oil absorbent is also due to Brégeat.[141] It is generally agreed that tetralin has a greater absorptive capacity for aromatic hydrocarbons than any other suggested wash oil.[142] Its high cost makes its use prohibitive in America, since, because of a relatively high

[130] The National Benzole Association, *Rept. Joint Benzole Research Com.*, **1929**, 86.
[131] The National Benzole Association, *ibid.*, **1928**, p. 124.
[132] Whittaker, F. D., *Gas World*, **78**, Coking Sect., 51–4 (1923).
[133] Pooley, H., *J. Gas Lighting*, **133**, 689–90 (1916).
[134] Curry, J., *Gas World*, **106**, Coking Sect., 39–44 (1937).
[135] Daniel, A., and Brégeat, J. H., Fr. Pat. 502,957 (1916); Brit. Pat. 128,640 (1916).
[136] Grebel, A., *Génie civil*, **75**, 445–52 (1919).

[137] Weissenberger, G., *Gas- u. Wasserfach*, **65**, 33–4 (1922).
[138] Porter, H. C., *Coal Carbonization*, Chemical Catalog Co., New York, 1924, p. 309.
[139] Berl, E., and Schwebel, W., *Z. angew. Chem.*, **35**, 189–92 (1922). Weissenberger, G., et al., *Kunststoffe*, **14**, 33–5 (1924); *Monatsh.*, **45**, 187–206, 281–5 (1924). The National Benzole Association, *Rept. Joint Benzole Research Com.*, **1926**, 138.
[140] Runge, W., and Curtis, H. A., U. S. Pat. 1,349,128 (1922). Brégeat Corp., U. S. Pat. 1,513,152 (1924).
[141] Brégeat Corp., U. S. Pat. 1,513,153 (1924).
[142] Weissenberger, G., et al., *Petroleum Z.* **20**, 1817–25 (1924); *Z. angew. Chem.*, **38**, 359–62, 626–9, 1161–4 (1925); *Glückauf*, **61**, 426–30 (1925); *Gas- u. Wasserfach*, **69**, 493–6, 528–31, 549–54 (1926); *Monatsh.*, **45**, 449–55 (1924). The National Benzole Association, *Rept. Joint Benzole Research Com.*, **1926**, 122, 139, **1928**, 110, 130, 147, 159.

vapor pressure,[143] appreciable quantities are lost to the gas. Tetralin has found some use as a solvent for naphthalene in distribution systems for manufactured gas.[144]

The resin oil obtained from the dry distillation of the resins of light-oil refining has been patented [145] as an absorbent medium. The suitability of similar oils has been discussed by Kattwinkel.[146]

THE WASH-OIL PROCESS FOR RECOVERY OF LIGHT OIL

THE SCRUBBER

Light-oil scrubbers can be divided into three main classifications: (1) tower scrubbers; (2) static washers, consisting of a horizontal assembly of four to eight scrubbing chambers, usually filled with a packing material which may be lathe turnings, expanded metal, brushes, porcelain rings, Berl saddles, etc.; and (3) mechanical washers, horizontal or vertical, and characterized by being provided with some mechanical means, such as revolving elements, for distributing the oil and continually bringing it into contact with the gas. There are a vast number of designs for static and mechanical gas scrubbers. Significantly, they have found application only at small installations, particularly at gasworks. Their only advantages seem to be a very low back pressure and, because of the relatively small height, the possibility of conveniently housing the apparatus in a building. The last consideration may be important at installations in hot climates. The countercurrent principle is usually violated to a greater or lesser extent; consequently, recovery efficiencies are low. The following descriptions are chiefly from Hoffert and Claxton.[6]

Tower Scrubbers. Most of the light oil now recovered, both in domestic and foreign practice, is removed from the gas in some sort of tower scrubber. In essentials, the tower consists of a tall cylindrical shell of steel, filled with a packing material and provided with suitable gas and oil inlet and outlet connections. Scrubbing towers are usually about six times as high as wide, and two or three units, with the gas flow in series, may be used. In modern practice, by employing effective packing, the number of scrubbers can be usually reduced to one or at most not more than two.

Although many types of packing have been described, such as coke, brushwood, earthenware pipes, Raschig, Lessing, and Prym rings, Berl saddle, Brégeat spirals, Foster and Jarvis baffles,[147] and expanded metal bundles,[148] in American practice the packing is usually either wooden hurdles or steel turnings. Wooden hurdles are fabricated of narrow boards, perhaps 6 inches wide by ¼ inch thick. The boards are assembled with the flat faces parallel, contiguous boards being separated by ½-inch spacers and the whole being held together with long bolts. The general effect is to produce a wooden grating providing a great many slots for the simultaneous passage of oil and gas. The length of the slots is equal to the length of the boards; the depth is equal to the width of the boards; the width depends upon the space between them. The circular hurdles so made are stacked in tiers on supports fixed to the

143 Platti, L., *Z. angew. Chem.*, **42**, 1035–6 (1929). Linder, E. G., *J. Phys. Chem.*, **35**, 531–5 (1931). Gardner, G. S., and Brewer, J. E., *Ind. Eng. Chem.*, **29**, 179–81 (1937).

144 Shea, M. E., *Am. Gas J.*, **148**, No. 4, 31–4, 53 (1938).

145 Concordia-Bergbau A.-G., Ger. Pat. 629,995 (1936).

146 Kattwinkel, R., *Brennstoff-Chem.*, **4**, 377–8 (1923).

147 Burrell, G. A., *The Recovery of Gasoline from Natural Gas*, Chemical Catalog Co., New York, 1925, pp. 209–11.

148 Reichard, F., *Gas- u. Wasserfach*, **80**, 38–43 (1937).

wall of the tower, the supports being 8 to 12 feet apart. There should be a definite gap between successive hurdles, since, if they are laid in direct contact, it is possible to have only about half the surface wetted. Frequently, the filling is so arranged that the boards in alternate tiers are at approximately 45° to each other. The lower, dripping edge of the boards is often serrated to provide some means of dividing the descending oil sheet into a large number of smaller streams. The material of construction is ordinarily redwood, white pine, or spruce. Wooden hurdle packing is usually designed to be readily removable for cleaning operations. Prolonged steaming *in situ* is not advisable.

Wooden hurdles possess the advantage of ready fabrication, easy repair, and a very low gas pressure drop. Unfortunately, the functional efficiency of hurdles as a packing material is low, and it is difficult to prevent extensive wall effects. A height per theoretical unit, HTU, of 20 feet is the best that is commonly realized under ordinary conditions.

A much more satisfactory solution to the problem is obtained through the use of steel lathe turnings. HTU's of about 10 feet can be readily attained in towers of 4-foot diameter or more, with corresponding gas velocities of 2.5 to 3.0 feet per second. The turnings, necessarily well sorted and cleaned, are supported on metal gratings (subway type), it being the usual practice to provide a separate support for each 10 feet of material. Such a packing, once in place, has a long life and can be subjected to very severe cleaning techniques. Turnings exhibit an excellent distribution of the wash oil, and channeling is but very rarely encountered.

The liquid absorbent is usually introduced through a large number of nozzles installed in the top of the scrubber. Fre-

quently, the nozzles are provided with a plate on which the oil jet impinges. Although much ingenuity has been expended in the invention of oil-nozzle devices,[149] it is preferable to employ some simple design incorporating provision for easy rodding and cleaning. Multiple-type nozzle designs are much used in American practice; a single central nozzle device due to Otto is popular abroad. In this apparatus a single large nozzle is supported directly above an arrangement of four or more coaxial, truncated, hollow cones of uniformly decreasing size. The highest cone throws part of the oil to the outside of the top of the packing surface while the rest of the oil passes, through a central opening, to the next and smaller cone. Here the process is repeated, the portion of the packing being irrigated lying again somewhat closer to the center line. The cones and openings require careful machining and setting for satisfactory operation.

Channeling in packed towers may be reduced by attaching inclined baffles at intervals to the walls or by arranging special lenticular plates within the packing so that the down-flowing liquid is directed from the sides toward the center.[150]

It is ordinarily convenient to include, in the base of the scrubber (utilizing the same shell), a benzolized oil storage tank of sufficient size to take up any irregularities in the rate of flow of oil through the debenzolizing still. In a similar utilization of the main shell structure a portion of the top of the tower is left empty to permit detrainment of oil from the gas. Although this scheme is usually adequate, it may sometimes be desirable to install an oil sepa-

149 Still, C., Ger. Pat. 329,118 (1920). Kuhn, A., U. S. Pat. 1,502,573 (1924). Cäsar, W., *Glückauf*, 61, 613–7 (1925).

150 Chem. Fabr. Curtius A.-G., Brit. Pat. 431,-788 (1934).

rator in the gas line leaving the light-oil scrubbers.

The effectiveness of tower scrubbers during use will gradually decrease with time owing to the formation of a deposit on the packing, the deposit being caused primarily by the accumulation of high-boiling coal-tar derivatives, altered, presumably, by oxidation and polymerization.[151] Cleaning may be facilitated by the circulation of hot alkaline solutions, unwashed solvent naphtha,[152] tar and tar fractions, emulsions of solvent naphtha, naphthenic acids, and water,[153] hot wash oil, and by simple steaming.

Bubble-cap column towers have the advantage of providing a positive intimate contact between gas and oil; the chief disadvantages are the high cost, large entrainment, and excessive back-pressure.[154] Bubble-cap columns have been used effectively at pressures of 5 to 8 atmospheres.[155] The scrubbing of gas at high pressures results in a small, compact absorber design but is usually employed only where compression of the gas is required for other purposes.

Tower scrubbers should be operated in a truly countercurrent manner. Recirculation of oil is inevitably accompanied by a loss of efficiency and is completely indefensible, except for deliberate partial recovery where the low wash-oil rate would not serve to irrigate the packing properly.[156] In modern tower scrubber design the latter contingency is encountered only in washing for naphthalene and gum formers. The use of recirculation can frequently be traced to an inadequate comprehension of the basic principles of gas washing. Recirculation in the debenzolizing system, with a view to the reduction of deposits, has been patented.[157] When great freedom from naphthalene is desired, or when a scrubbing action more intensive than that obtained by large oil-to-gas ratios and the use of a practical degree of debenzolization is required, gas washing with debenzolized oil may be supplemented by a final treatment with a small quantity of *fresh* wash oil.[158]

STATIC WASHERS

The Livesey washer, a World War I expedient, consisted of a double trough, the lower section being perforated and the upper serving as a gas offtake. The gas entered the washer at the bottom, was dispersed by passing through the perforations, and then bubbled through the oil. This apparatus was unique in the combination, in one design, of most of the undesirable features possible in a gas-washing device.

The "Stator" washer (Newton Chambers & Co. [British]) shown in Fig. 11 consists of a cast-iron or mild-steel box through which the gas passes longitudinally. The box is divided into a series of compartments at right angles to the path of the gas. These compartments are filled with Raschig rings, or any impervious packing that gives the maximum surface per unit volume and the least back-pressure. At the base of each compartment is a trough for collecting the wash oil. Between each pair of such troughs is an interconnecting trough, from which the liquid is pumped and distributed evenly at the top of the next compartment. • • • Apertures are arranged in the divisions between the troughs at the base of each washing compartment and the adjacent interconnecting troughs, so that some of the liquid from each washing trough flows backward into the preceding interconnecting trough, and some forward into the succeeding interconnecting trough. Portions of the liquid are thus re-

151 See Pannertz, F., in ref. 80.

152 Wysehall, J. M., and Empson, G. L., *Gas World*, **81**, 78–9 (1924).

153 Brodovich, A. I., and Faingold, S. G., *Chimie & industrie*, **41**, 466 (1938); *Coke and Chem. (U.S.S.R.)*, **8**, No. 6, 33–4 (1938).

154 Adam, W. G., and Anderson, G. W., *Gas World*, **105**, 6–10 (1936).

155 Demann, W., *Glückauf*, **73**, 593–605 (1937).

156 Barritt, R. J., *Gas World*, **115**, Coking Sect., 10–1 (1941).

157 Wilton, T. O., and Mann, H. C., Brit. Pat. 499,332 (1937).

158 Becker, J., U. S. Pat. 1,760,335 (1930).
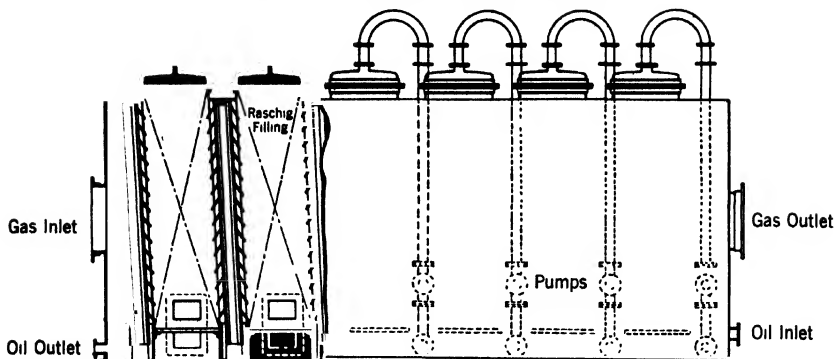
Fig. 11. "Stator" washer of Newton Chambers and Company.[6]

circulated in the apparatus, thereby increasing its efficiency, and bypassing of the liquid is eliminated. • • • For a gas make of 3,000,000 cubic feet per day the makers supply a washer approximately 18 feet long, 4 feet wide, and 8 feet high.[6]

The Wilton's double-bay gas scrubber shown in Fig. 12 consists essentially of a compact series of tower scrubbers, the oil and gas flow within each tower being *concurrent*, although the overall arrangement of the towers is countercurrent. Eight compartments are used. "Each compartment has both a down-take and an up-take for gas, the former being fitted with a special spiral filling consisting of tubes containing twisted metal strips. The up-take prevents entrainment of oil from one bay to the next. Each bay is provided with its
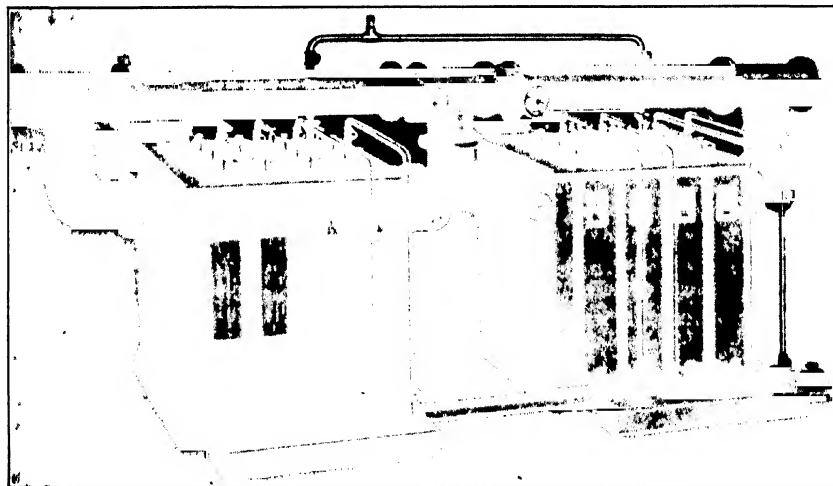
Fig. 12. Wilton's double-bay gas scrubber.[6]

own pump for circulating the oil up to the spray and down through the filling to the well again. The oil from one bay overflows internally to the next bay." In contrast to the conditions in a tower scrubber, the leanest gas does not come in contact with freshly debenzolized oil. Wearing has stated [75] that multibay washers are desirable where it may be frequently advisable to change to partial scrubbing for naphthalene alone. This advantage seems to be somewhat dubious; Powell [159] has described the successful use of packed towers for the removal of naphthalene and gum formers.

Similar multibay washers are manufactured by Holmes,[160] Simon-Carves, and H. Koppers.[155] C. Otto and Company [155, 161] constructs a multibay washer with the stages placed one above the other; the external appearance counterfeits that of a tower washer. Each stage is packed with specially formed metal "Intos" hurdles.

MECHANICAL WASHERS

Incorporation of some form of motor-driven moving element designed to bring about an intimate contact between oil and gas characterizes mechanical washers, which may be readily classified into vertical, horizontal, and centrifugal types.

In the "Triumph" *vertical* washer-scrubber (Fig. 13), the apparatus is divided into six or more vertically superimposed chambers.

In each chamber, the packing material, consisting of small thin rings, is carried on an expanded-metal tray, below which is fitted an oil-collecting tray on the underside of which is a series of projections. The washer is fitted with a central vertical shaft, on which is mounted in each chamber a circulator,

which picks up oil from the collecting tray and causes it to impinge upon the projections on the collecting trays immediately above, thus ensuring a uniform distribution of the oil over the whole area of the packing material. The gas in the scrubber is also effectively washed by spray in the free space above the packing. The oil in each chamber is circulated continuously through the scrubbing-medium, and the rate of oil flow through the washer is regulated by the feed to the top chamber, the oil overflowing from tray to tray.[6]

The rotary washer of Martini-Huneke [155]. is of this type.

In the Holmes *horizontal* rotary washer (Fig. 14)

there is an outer cast-iron cylindrical casing varying from 8 to 12 feet in diameter according to capacity. It is divided into a number of compartments through which passes a horizontal shaft to which are attached double circular brushes occupying the whole width of a chamber. This flexible brush-filling is the chief feature of the Holmes washer. The lower part of each compartment contains wash oil, through which the whole of the brush passes at each revolution of the main shaft. The debenzolized oil is admitted at the gas-outlet end and overflows from chamber to chamber, thus passing through the washer countercurrent to the gas. The saturated oil finally leaves the washer at the gas-inlet end. The gas enters the first chamber of the washer, and travels through both sides of the double brush, from the outer circumference inwards to the gas space surrounding the shaft and thence into the next chamber, and then outwards to the gas space situated between the brush and the washer casing. The saturation of the wash oil with benzole, thus, becomes higher in each successive compartment. Owing to the lightness of the brush filling, only two external bearings, one at each end of a unit, are required to support the main shaft.[6]

The rotary scrubbers built by various English and continental manufacturers vary but little from the above, differing chiefly in the detailed design of the rotated packing and in the incorporation of special

159 Powell, A. R., *Proc. Am. Gas Assoc.*, **1935**, 699.

160 Holmes, W. C., and Co., Brit. Pat. 331,818 (1929).

161 Berthelot, C., *Rev. mét.*, **35**, 439–47, 509–22 (1938).

Adjusting Nuts
Roller Bearing
Ball Thrust Bearing

Access Door to
Stuffing Boxes

Washing Chamber

Washing Chamber

Washing Chamber
Sight Hole
Inspection Door

Washing Chamber

Liquor Drain

Test Tar

Washing Chamber

Inspection Chamber
Coupling
Roller Bearing

Gasway

Inspection Cover
Hinged Door to
Inspection
Chamber

Washing Chamber
Special M.S Ferrule
Filling
Liquor Distributor
Washing Chamber

Washing Chamber

Washing Chamber

Washing Chamber

Inlet Chamber

Roller Bearing
Bevel Gears
Enclosed Oil Bath

Enclosed
Steam
Engine
Pressure
Lubrication
Type

FIG. 13. "Triumph" vertical washer-scrubber.[5]

1188

devices, such as small buckets welded to the rotating elements, to provide for a more equable distribution of the oil. According to Souders and Brown, rotary scrubbers are suitable for the extraction of about 70 percent of the light oil in the gas.[72]

Vertical *centrifugal* scrubbers have found some application in light-oil recovery. In this type of washer, the gas is scrubbed by

the Bartlett Hayward Company of Baltimore. English designs include the Davison-Liversedge by W. C. Holmes and Company and the "Spiral Standard" by Kirkham, Hulett, and Chandler. In the last, the gas inlets and outlets to each chamber are arranged so that the flow of the gas through the machine describes a giant helix. The oil spray in each chamber is formed by a vertically mounted centrifugal pump
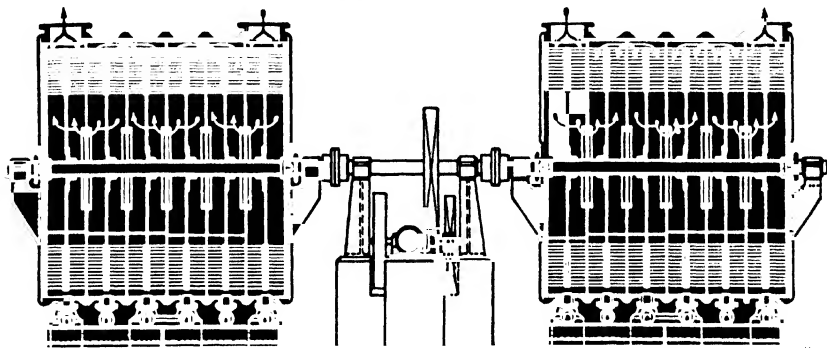
FIG. 14.   Horizontal rotary scrubber of W. C. Holmes and Company.[a]

the oil in the form of a fine spray in six or more superimposed sections or chambers, through which the gas ascends in turn. The spray is produced by suitably designed elements attached to a rapidly revolving vertical shaft (200 rpm or more). Most of the sprayed oil is re-collected; it returns to the same well and is again thrown outward. A surplus, depending upon the oil feed to the system, overflows to the next lower tray. The absorption process is countercurrent in the main, but obviously much recirculation takes place.

The Feld [162, 163] washer (Fig. 15), the prototype, is manufactured in America by

162 Funcke, W., *Glückauf*, **60**, 835–40 (1924).
163 Gluud, W., and Jacobson, D. L., *International Handbook of the By-Product Coke Industry*, Chemical Catalog Co., New York, 1932, 879 pp.

bounded by a perforated basket. The tangential oil spray may be caused to flow with or against the stream of gas; flowing against it produces a somewhat higher back-pressure. Oil separators are usually mandatory when centrifugal washers are used.

THE DEBENZOLIZING SYSTEM

In the debenzolizing plant the engineer is faced with the problem of separating a relatively small amount of light oil from a relatively large amount of the absorbing medium. This, in both domestic and foreign practice, is accomplished through some application of fractional distillation. It is desirable, in the initial step, to effect as sharp a separation as possible; that is, the light oil should contain the minimum ad-

mixture of wash oil and the stripped wash oil should retain no significant amount of light oil. The complete removal of the more volatile constituents is easy; the separation becomes increasingly difficult as

FIG. 15.   Centrifugal Feld washer.[165]

the boiling points of the desired constituents approach those of the low-boiling constituents of the wash oil. With some liquid absorbents of low boiling point it may be found that very appreciable loss of the absorbent to the light oil will occur. It is general practice, at recent installations, to operate in the primary debenzolizing step

so that the debenzolized wash oil is relatively free of light oil and to accomplish the removal of the "carryover" wash oil by subsequent rectification of the crude light-oil product.

The debenzolization of wash oil by simple fractional distillation at atmospheric pressure (without the use of an inert sweeping component) has found little application. The high temperatures necessary are technically difficult to obtain without gas-fired pipe-stills, which are notoriously expensive to maintain and operate. Further, the high temperature to which the wash oil must be heated results in a rapid degradation of the scrubbing medium. Krautwurst has described the Pintsch process,[164] operating on this principle. Decomposition of the wash oil is claimed to be avoided by the use of a specially designed gas-fired tube heater.

A natural extension of fractional distillation at atmospheric pressure is the introduction of systems operating at reduced pressures; in such vacuum debenzolization plants, the wash oil need not be heated above 140° C. Most of the installations have been confined to continental practice, particularly in the period from 1922 to 1928. There is considerable lack of agreement as to the relative merits and demerits of the vacuum debenzolization plant in comparison with the straightforward steam distillation process. A most significant commentary is the reluctance of the operator of a modern light-oil plant to install reduced-pressure debenzolization systems. Among other disadvantages one may mention: large initial investment costs, high maintenance charges, complexity and difficulty of operation, and the necessity of ensuring freedom from air leakage. Very adequate descriptions will be found in the

164 Krautwurst, F., *Gas- u. Wasserfach*, **79**, 838–40 (1936).

rather abundant literature.[165] The theoretical aspects of vacuum debenzolization have been discussed by Robinson and Gilliland.[166]

It is readily conceivable that a compromise process involving steam distillation under reduced pressure might possess practical advantages. It would seem that the degradation of the scrubbing medium directly due to heating might be distinctly reduced. Installations of this type have not yet been introduced into American practice.

The modern light-oil plant utilizes steam stripping at substantially atmospheric pressure. The benzolized wash oil, suitably preheated by heat exchange and additional steam, is introduced into the top of a multiplate bubble-cap column down which it flows countercurrent to an ascending stream of steam. Leaving the base of the column, the debenzolized oil, after separation of water and cooling, is returned to the top of the light-oil scrubbers. The vapors leaving the debenzolizing column, consisting of light oil, steam, and some wash oil, are condensed, cooled, and the water separated, the cooled light oil running to storage. This is the simplest type of installation and may be frequently modi-

165 Hartman, A., Ger. Pat. 298,823 (1913). Berl, E., and Schwebel, W., ref. 139. Raschig, F., *Gas- u. Wasserfach*, **65**, 655–8 (1922) ; *Z. angew. Chem.*, **40**, 1089–90 (1927). Neumann, B., *Glückauf*, **60**, 71–5 (1924). Kelting, M., *ibid.*, **60**, 176–8 (1924). Bähr, H., and Rühl, G., *ibid.*, **61**, 574–80 (1925). Hilgenstock, O., *Brennstoff-Chem.*, **7**, 87–9 (1926). Gareis, *Gas- u. Wasserfach*, **69**, 269–72 (1926). Fitz, W., *Teer*, **24**, 485–9 (1926). Schmalenbach, A., *Glückauf*, **62**, 45–50 (1926). Kattwinkel, R., *ibid.*, **62**, 529–34 (1926). Fichoux, A., *Chimie & industrie*, Spec. No., 292–307, April, 1928. Soc. des établ. Barbet, Brit. Pat. 381,429 (1932). Krebs, O., *Teer u. Bitumen*, **30**, 15–9, 29–33 (1932). Hollings, H., Hutchison, W. K., and Griffith, R. H., *Gas J.*, **220**, 475 (1937).

166 Robinson, C. S., and Gilliland, E. R., *The Elements of Fractional Distillation*, McGraw-Hill Book Co., New York, 3rd ed., 1939, 267 pp.

fied by the interposition of various rectifiers in the vapor stream. The function of these units is to effect a further elimination of the wash oil from the crude light oil, to prepare a light oil of definite maximum dry point, etc. The separation of a complete light-oil plant into a purification plant and a debenzolizing plant is somewhat arbitrary; the purification plant may be thought to begin with that apparatus wherein an attempt is made to separate the benzol-toluol-xylol portion of the light oil into two or more fractions.

Probably no two light-oil-recovery plants in existence are identical in the detailed disposition and utilization of apparatus; in general, the complexity increases with the size of the plant. A generalized description typical of modern American practice will be given here. Constructed in 1940, the plant was designed to handle a wash-oil circulation of 50,000 gallons per hour, the auxiliary refining equipment being capable of treating 24,000 gallons per day. Figure 16 presents the flow diagram of the crude light-oil system; Fig. 17 is a general view of the actual physical installation.

The benzolized wash oil draining into the base of the tower scrubbers is transferred, by means of centrifugal pumps, to a 50,000-gallon surge tank. From this tank (not shown in the flow diagram) the benzolized wash oil is pumped, again by means of an all-iron, centrifugal, steam-driven pump, to the vapor-to-oil heat exchangers, the preheaters, and, finally, the stripping stills.

In this particular installation, because of its size, and other considerations, it was desirable to construct two stripping stills operating in parallel. As a corollary to this design, each still is provided with a separate heat-exchange and preheating system.

The vapor-to-oil heat exchangers are of the drip type, having a rectangular steel

Fig. 16. Flow diagram of a typical modern light-oil-recovery plant.

shell, three banks of tubes, and fixed tube sheets. The cold benzolized oil enters at the bottom of the apparatus, flowing within the tubes, and is heated by the mixture of steam and light-oil vapors flowing downward in the space around the tubes. The temperature conditions in the vapor-to-oil heat exchanger are so regulated that a major portion of the steam is condensed, this steam condensate being accompanied by a small amount of "primary light oil," which is substantially wash oil containing only small amounts of light-oil constituents. The aqueous and oily condensate is fed to a gravity separator where an appropriate separation is made, the water going either to waste or to a contaminated water sump for further separation. In small plants the "primary light oil" may be returned directly to the benzolized wash oil; in this plant the primary light oil is introduced on the appropriate tray of the light-oil rectifier.

In some plants of recent design oil-to-oil heat exchangers have been used with considerable success. Occasionally, both vapor-to-oil and oil-to-oil apparatus will be found in one system. The reluctance to use oil-to-oil interchangers may be traced, in part, to the difficulty of detecting leakage between the benzolized oil stream and the debenzolized oil stream and to the difficulty of cleaning the heating surfaces. An oil-to-oil heat exchanger is mandatory if the debenzolization step is carried out at high temperatures.

It is important to note that, in the flow diagram illustrated, the vapor-to-oil heat exchange has a dual function. One purpose, of course, is to recover heat that would otherwise be lost; the other is to act as a partial condenser and thereby partially dehydrate the vapors leaving the wash-oil still. The control of the temperature of the vapors leaving the vapor-to-oil

Fig. 17. Modern light-oil-recovery and semi-continuous refining plant.

exchanger is somewhat critical and is occasionally effected by bypassing some of the oil around the exchanger.

Since complete heat interchange can never be obtained, the benzolized oil, after leaving the vapor-to-oil heat exchanger, enters a final heater, where, in this installation, its temperature is raised to approximately 120° C. Final heaters are usually of the shell-and-tube type, with oil flowing through the tubes, and with the steam, or other heating medium, on the shell side. Since some distillation will occur in the final heater the wash-oil outlet is usually made somewhat larger than the wash-oil inlet. The final heaters, vapor-to-oil interchangers, and the hot oil and vapor piping are ordinarily effectively insulated.

The hot benzolized oil now enters the top, or near the top, of the stripping column, whence it flows downward countercurrent to upflowing steam. At this installation, there are two identical wash-oil stills, each essentially a cylindrical shell 8 feet in diameter and 45 feet high, the interior being fitted in the conventional manner with a plurality of bubble-cap trays. In modern practice, columns of this size are

usually of all-welded sheet-steel construction, the shell and tray plates being of ⅜-inch material. Each tray is fitted with 50 to 100 cast-iron Sterling bubble caps and is provided with inlet and outlet weirs and suitable means for conveying liquid from each tray to the tray below. It is conventional to introduce the hot oil not on the top tray but on a suitably chosen lower tray, the upper dry trays effectively preventing any entrainment of oil. Much of the operating efficiency of wash-oil stripping columns depends upon the skill of the erecting engineer: it is quite essential that all the bubble caps on each tray be at the same height and that the trays be precisely level. The base of the still is left empty to serve as a hot-oil drain tank. The hot debenzolized oil from the last tray flows to the still compartment, essentially a small reservoir, and from there to the hot-oil drain tank in the base of the still. Both the still compartment and the hot-oil drain tank are provided with automatic liquid-level regulators.

The wash-oil purifier is of the Stover [85] design, and all the direct steam entering the base of the still first passes through the hot oil held in the shell of the purifier. The consumption of direct steam is a function of the degree of debenzolization required; it is common to use 0.6 to 0.8 pound of direct steam per gallon of wash oil stripped.

The hot debenzolized oil in the hot-oil drain tank is then pumped through the wash-oil coolers to the decanter tank and from there to a wash-oil circulating tank. From this reservoir the now cold debenzolized oil is again sprayed into the top of the light-oil scrubbers, where it begins the cycle anew.

The wash oil can be cooled in many ways. The most common American design consists of many banks of horizontal runs of pipe connected with return bends and placed, vertically, one above the other. Water from a perforated pipe or from a trough is caused to flow on the top run of pipe, whence part of it trickles down over the whole bank. Frequently, cast sections are used, the lower edges of the pipes being provided with a drip strip ("gilled"). In such a device the hot oil first enters the lowest run of pipe and zigzags to the top, the contact between oil and water being crudely countercurrent. Some evaporative cooling takes place. Recent installations show evidence of a tendency away from designs fabricated in the field from standard pipe towards the use of apparatus assembled, in multiple units, of devices specifically designed for the purpose of heat exchange by the specialists in the art.

Thau [167] has described the wash-oil cooling practice of continental designers. In addition to the horizontal trough coolers described above, use is made of tubular coolers, shell-and-tube coolers, box coolers, and direct coolers, the last representing a distinctly European practice, few examples being found in America. Tubular coolers consist of a grid of tubes, each tube surrounding a narrower tube or a nest of tubes through which water flows. The oil flows from the top to the bottom of the grid, through the annular space surrounding the water tubes, countercurrent to the direction of cold-water flow. Shell-and-tube coolers are similar, usually consisting of only one nest of tubes within a large shell. Box coolers, or flat coolers, are constructed in the shape of very narrow boxes about 23 feet long, 5 feet high, and 1.75 feet wide. Water passes through tubes placed in the boxes, the hot oil flowing approximately countercurrent in the surrounding space.

In direct coolers the hot oil is brought

167 Thau, A., *Glückauf*, 57, 1165 (1921).

into direct contact with cold water. In some systems the two fluids are caused to flow more or less quietly in countercurrent contiguous layers. In other designs intimate mixing is employed; heat transfer is then more complete, but there is, unavoidably, a greater tendency towards emulsification. The satisfactory operation of direct coolers requires careful supervision [168] and the use of a low-free-carbon [169] oil, preferably predominantly paraffinic and having a specific gravity widely different from that of water. Many designs have been described.[170]

In the stripping tower the hot oil flowing downward comes into countercurrent contact with steam vapor blowing upwards. The process of stripping can be considered simply as the inverse of absorption, and the calculations and diagrams differ from those of absorption only in that the operating line lies below the equilibrium curve rather than above it. It is obvious that as the steam vapors flow upwards their volume increases, owing to the stripped light oil. Hence, the gas-volume flow increases progressively up the column. It is naturally advantageous to operate with as low a pressure and as high a temperature as possible. In the theoretical case of complete stripping, the steam consumption is directly proportional to the total pressure and inversely proportional to the Henry's law

constant at the operating temperature. Further, the steam consumption for *total* stripping is independent of the concentration of light oil in the benzolized oil; the steam necessary for complete stripping is simply that computed for the least volatile component, just as though the others were not present.[171] The concentration of light oil in the wash oil will naturally vary with the oil-to-gas ratio, higher ratios producing a more dilute solution of light oil in the wash oil. In partial stripping, the steam requirement for stripping will vary, although not directly, with the oil-to-gas ratio. The graphical stepwise procedure employed for calculation of the absorption can also be applied to determine the number of theoretical stripping trays necessary; this value when related to the number of actual trays may be used to define the plate efficiency of the stripping still. An average value of 70 percent is common.

The mixture of light-oil vapors and steam leaving the base of the vapor-to-oil heat exchangers enters at the approximate middle of the light-oil rectifier. The purpose of the rectifier is to separate the light oil into two fractions, one a secondary light oil comprising benzol, toluol, xylol, and solvent up to any predetermined dry point, and the other an intermediate light oil containing heavy solvents, naphthalene and wash oil.

In the installation being described, the rectifier is 8 feet in diameter by approximately 20 feet high, is constructed of 5/16-inch steel plate, and is provided with an approximately equal number of stripping plates (below the feed) and rectifying plates (above the feed). The trays are of the bubble-cap type, and, in addition, those in the stripping section are fitted with

[168] Schneider, F., *Z. Ver. Gas- u. Wasserfach.*, **61**, 109–11 (1921).

[169] Buckley, W. E., Bradley, G. W. J., Greenfield, G. J., and Ruddy, R. H., *Gas World*, **104**, Coking Sect., 47–50 (1936).

[170] Ibing, H., Brit. Pat. 176,499 (1920); Ger. Pat. 395,205 (1924). Jungeblodt, E., Ger. Pat. 355,990 (1921). Goldschmidt, F., and Ott, A., Ger. Pat., 383,674 (1921). Otto, C., and Co., Ger. Pats. 368,416 (1921), 479,954 (1925). Kuhn, A., *Chem. & Met. Eng.*, **26**, 32 (1922). Still, C., Ger. Pats. 382,862, 385,060 (1923), 453,715 (1927). Werner, T., *Gas- u. Wasserfach*, **67**, 49–51 (1924). Klemstedt, H., *ibid.*, **67**, 406–7 (1924).

[171] Walker, W. H., Lewis, W. K., McAdams, W. H., and Gilliland, E. R., *Principles of Chemical Engineering*, McGraw-Hill Book Co., New York, 1937, 749 pp.

steam coils, arranged for immersion in the liquid on the tray.

Rectification is brought about by the introduction, on the top tray of the rectifying section, of a reflux stream of secondary light oil, the condensed product. The amount of reflux is automatically controlled by the temperature of the vapors leaving the column. The water vapor originally present in the feed is usually almost completely condensed, through direct heat interchange, on the first tray of the rectifying section, and provision is made for draining this condensed water to the primary light-oil separator. The separated oil is returned, from this device, to the first tray of the stripping section of the rectifier. The primary light oil from the vapor-to-oil heat exchangers also enters this separator and is eventually fed to the first stripping tray of the rectifier. As previously mentioned, other disposition is frequently made of the primary light oil. The rate of removal of intermediate light oil from the base of the rectifier is automatically controlled by a suitable liquid-level regulator.

The rectified vapors pass to the light-oil condenser, usually of the drip type, designed as a rectangular, steel-plate shell with several banks of tubes. The flow of cooling water and vapors is approximately countercurrent, the vapors entering the top, the cooling water entering the bottom. The condensed and cooled light oil flows to a gravity separator where substantially complete removal of nondissolved water is accomplished. A portion of the light oil is diverted to the rectifier as reflux; the rest flows to storage tanks, where it serves as the process raw material for the refining section of the plant.

The intermediate light oil is accumulated and periodically charged to a batch rectifying still, where the material is fraction-ated under a mild vacuum to secondary light oil, heavy solvent, naphthalene, and wash oil. The secondary light oil and wash oil are returned to the appropriate parts of the system; the heavy solvent and naphthalene are sold in various crude grades. When desired, the same still can be used to refractionate the crude solvents and naphthalene to closer-boiling cuts of increased value and marketability. The crude batch still is provided with the appropriate still tank, condensers, separators, receiving tanks, and vacuum pumps.

Inasmuch as the light-oil rectifier can be operated to produce a light oil of any dry point, it is readily apparent that the plant can be operated to include most of the styrene cut in the intermediate light oil. With apparatus of such flexibility the light-oil-plant operator is in a position to produce materials hitherto not offered to the market by the light-oil industry.

Although the above description may be taken as typical of a modern debenzolizing plant, it must be recognized that an enormous number of variants exist. The details of any particular system depend largely upon the size and age of the installation. For example, hot and cold oil decanters were once widely used, although few examples are now seen. In these devices a spray of water was forced through the oil held in a suitable tank. A certain amount of muck collected at the oil-water interface and was periodically removed. This method of maintaining oil quality was often made difficult by the formation of troublesome emulsions. The hot-oil decanter also acted as a direct cooler.

In the simplest type of plant, usually no attempt is made to rectify the crude light oil; such a plant consists of a steam stripping still and little else. The crude light oil necessarily contains a large amount of wash oil unless the steam stripping is delib-

erately ineffective. Usually, in the larger plants, some rectification of the crude light oil is carried out, and designs differ largely only in the extent to which this is done and in the type of apparatus employed. Various models of dephlegmators and packing-filled rectifiers are common in the older plants. Adequate detailed accounts of many of these systems have been given by Gluud [168] and by Hoffert and Claxton.[6]

Tiddy and Miller [5] have described a debenzolizing plant utilizing two continuous rectifiers. The vapors from the wash-oil still pass directly to a dephlegmator-type vapor-to-oil heat exchanger, the hydrocarbons condensing here being drained to a wash-oil-recovery tank. The vapors leaving the dephlegmator flow

to the base of the crude residue separating column where the vapors are separated into two fractions by means of a light oil reflux flow pumped to the top of the crude residue separation column [rectifier], countercurrent to the upflow mixture of vapors of light oil and water entering the base of the crude residue separating column. The higher-boiling constituents, which have condensed, flow from the base of the crude residue separating column to the residue stripper [second rectifier] where they are freed from any light-boiling fractions and flow from the residue stripper to the crude residue storage tank. The vapors leaving the crude residue separating column pass to a light oil condenser wherein they are condensed to a liquid state, flow to a light oil decanter for separation of any water, and overflow from the decanter to light oil storage. Part of the light oil flowing from the light oil decanters is often used for reflux to the crude residue separation column.

The vapors from the crude residue stripper enter the crude residue separating column at a point somewhat above the feed of vapors from the dephlegmator heat exchanger. The two crude residue columns fulfill the same function as the light-oil rectifier in the flow diagram first described.

These authors [5] presented the following table as typical of modern recovery operations in a light-oil plant.

Temperature of gas entering scrubbers	20–25° C
Temperature of wash oil entering scrubbers	22–27° C
Temperature of wash oil entering stripping still	135° C
Wash oil circulated per ton of coal carbonized	175–200 gallons
Fresh wash-oil make-up per 10,000 gallons of wash oil circulated	2.5–4.0 gallons
Light oil recovered per ton of coal carbonized	3.0–4.0 gallons
Enrichment of wash oil leaving scrubber	2.0–2.3 percent
Steam per gallon of wash oil circulated (atmospheric pressure operation)	0.50–0.75 pound
Light-oil recovery from coke-oven gas, average yearly rate	95 percent

Occasionally, unusual conditions demand novel treatment in the design of a light-oil plant. The Koppers Company installed a light-oil-recovery plant at an undertaking where the existing steam-generating facilities were grossly inadequate for conventional design. The construction of the needed boiler capacity would have raised the costs to a prohibitive level and vitiated the feasibility of the whole project. The problem was solved by using gas-heated Dowtherm, both as a vapor and as a liquid, wherever indirect steam would ordinarily be used. The consumption of direct steam in the stripping still was reduced to a very small quantity by carrying out the debenzolizing step at a temperature of 200° C. A hardwood distillate was added to the wash oil to prevent deterioration at this high temperature.

Lusby and Utermohle have described an interesting application of high-temperature

stripping to light-oil recovery at a gas plant. Emphasis in design was placed on the removal of styrene and indene from the gas. The process included the use of a hardwood distillate and a clay filter. The oil was heated by a direct-fired pipe still.[83]

THE PURIFICATION PLANT

The presence of benzene in coal tar was demonstrated in 1834 through the formation of aniline by H. W. Hoffman, who did not, however, effect any separation of the hydrocarbon from the mixture. The first refining of light oil, that is, the separation of light oil into substantially pure components, was carried out on coal-tar light oil by Mansfield in 1849.[172] His procedure involved washing with a solution of sulfuric acid, separation of the acid layer followed by a water wash, a caustic wash, another water wash, and finally a dry distillation of the washed oil. The procedure in modern technology does not differ in any significant way. Mansfield effected a final purification of his benzol by recrystallization; this process is today employed in the manufacture of most of the reagent benzol in use.

Modern refining practice is essentially confined to a combination of effective fractional distillation and treatment with sulfuric acid. The order of these operations depends upon the equipment of the refinery and the demand for particular grades of materials. In the recent past it has been the custom to subject the total light oil to a rigorous treatment with acid, the washed material being then separated by fractional distillation. A large part of the benzol fraction produced in this way was sold as motor fuel. Such a refining scheme was more or less mandatory since the coexisting motor-fuel specification contained a

clause defining the maximum tolerable discoloration as produced by the interaction, under certain test conditions, of the finished product with sulfuric acid. The acid-washing treatment was eminently successful in removing the conjugated diolefins and the other gum-forming constituents that contribute to the unsuitability of crude benzol as a motor fuel in internal-combustion engines. Concomitantly, most of the nongum-forming unsaturates were unfortunately also removed, these unsaturates being characterized by high heats of combustion and effective anti-knock ratings. It was early recognized that a prime desideratum would be a refining process that would remove, or render innocuous, the gum-formers, while retaining the bulk of the desirable unsaturated hydrocarbons. A large number of processes have been developed to accomplish this end; the inhibitor process is most common in American practice. The advent of milder motor-fuel-refining techniques saw the introduction of more realistic motor-fuel specifications, and they now frequently bear some relation to the functional properties of the material defined.

As a result of the use of the inhibitor process, or similar processes, it is now common to carry out some physical separation of the bulk light oil by fractional distillation prior to the application of chemical techniques such as acid washing. Frequently, a crude forerunnings fraction, a crude benzol fraction, a crude toluol-xylol fraction, and a crude solvent fraction will be obtained; the toluol-xylol cut and as much of the benzol as is needed for nitration material alone may be chemically refined.

Refining plants can be roughly classified, on the basis of the fractionating equipment, as batch plants, semi-continuous plants, and continuous plants. Designs in

172 Mansfield, C. B., J. Chem. Soc., 1, 244–68 (1849).

which all the physical separation is carried out in batch columns have long been obsolescent and require no further elaboration. In the semi-continuous .type of plant, the light oil is first separated into a few well-defined cuts by continuous fractional distillation in columns of appropriate design. The continuous columns are supplemented by one or more batch stills in which a large variety of special "pure" materials may be made. Usually continuous equipment is provided for the separation of forerunnings, motor benzol, and a fraction containing the toluol, xylol, and solvent present in the original material. The toluol-xylol-solvent cut is treated chemically and separated into components of the desired specifications by discontinuous distillation in the batch stills. The semi-continuous type of design combines economy with flexibility. The last characteristic is of significant importance in a market that constantly demands materials to new and varied specifications.

The continuous type of design provides enough columns so that the major components of light oil, particularly forerunnings, motor benzol, nitration benzol, toluol, and xylol, are separated systematically by continuous fractional distillation. In substance, the continuous plant differs from the semi-continuous only in the number of continuous columns, since even "continuous" plants must be supplemented by at least one batch still. The degree of continuity is merely a matter of definition; it would not be practicable to supply a column for every product that the light-oil-plant operator may be asked to prepare. In general, a multiplicity of continuous columns is feasible only in very large installations.

The proper design of a refining plant depends largely upon the size of the installation, local market opportunities, the geographic relation of the plant to other refining units in the same organization, and the nature of the refining equipment of large consumers. It is frequently desirable for small works to restrict refining on the premises to the production of motor fuel that can be sold locally, the rest of the light oil being shipped to a large central purification plant.

Although practically all light-oil-refining plants are similar variations on the two themes of acid washing and fractional distillation, a large number of detailed differences are found. In the following, the delineation in the main will be restricted to a description of a typical, modern, semi-continuous plant and a similarly modern continuous system, the discussion being centered about Figs. 18 and 19.

THE SEMI-CONTINUOUS PLANT

The general layout and flow diagram of the fractionating section of a typical semi-continuous plant of moderate size (12,000 gallons of light oil per day) are shown in Fig. 18.

The crude light oil, previously rectified to remove most of the heavy ends, enters the forerunnings column somewhat below the middle. The forerunnings stripper system includes the bubble-cap column proper, a condenser, water separator, reflux pump, flow meters, a reboiler, an automatic base-liquid-level control, and suitable temperature and pressure controls.

The function of the forerunnings stripper is to effect as complete a separation as possible between the forerunnings and the balance of the light oil. Ideally, the top product consists only of the components of the feed that are more volatile than benzene, the bottom product containing *all* the benzene and the less volatile constituents.

The column is operated under a slight constant back-pressure, and the noncondensables escape through an automatic pressure-regulating valve adjusted to maintain a desired constant pressure on the condenser vent. The noncondensables, that is, of vapors, the maximum amount of liquid product obtainable being mainly a function of condensing facilities.

The boil-up, or rate of boiling, and hence the rate of reflux return, is automatically regulated by a conventional-type tempera-
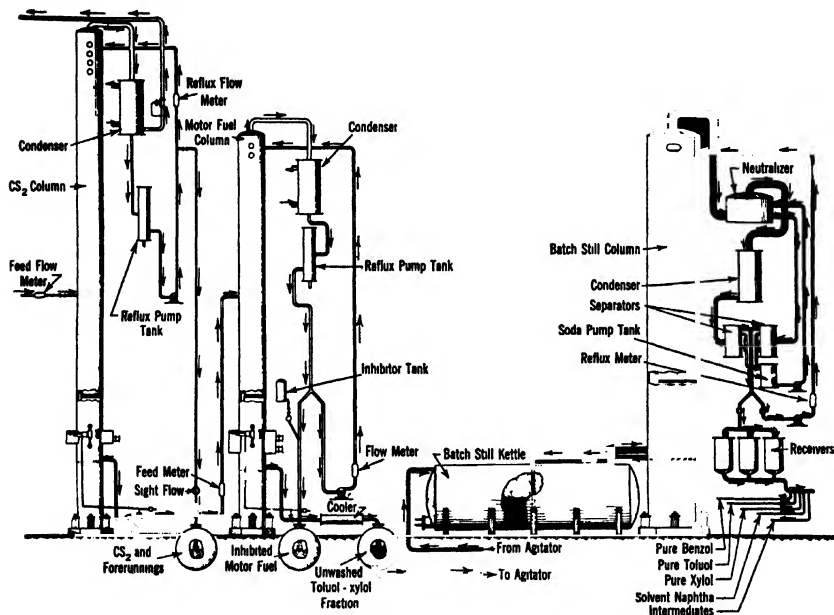
FIG. 18.   Flow diagram of a semi-continuous light-oil-recovery plant.

the hydrogen sulfide, methyl mercaptan, butadiene, butylenes, and other light-boiling constituents that remain in the vapor phase at the condenser conditions of temperature and pressure, are bled continuously into the fuel-gas main supplying the ovens. The liquid-phase forerunnings, usually in small volume, are continuously drawn off through a small manually controlled valve on the reflux pump discharge line. It is possible, by appropriate control of reflux condenser temperatures, to return all the forerunnings to the gas in the form

ture controller, the operating bulb being placed on a "sensitive" tray in the column. The continuous recording of tray temperatures at several points between the top and bottom of the column is eminently desirable. By directing suitable attention to thermal conditions, the operation of the column by means of analyses of the product can be held to a convenient minimum.

The installation and operation of continuous columns for the primary purpose of preparing forerunnings as a product are not at present economically feasible; fore-

runnings columns are justified by their beneficial effect on the nature of the motor benzol. Modern inhibited (unwashed) motor-fuel specifications contain clauses relating to corrosion and total sulfur content; the inclusion of forerunnings in the benzol fraction very often results in an unsatisfactory material. The complete removal of hydrogen sulfide and carbon disulfide that is possible by the use of modern forerunnings columns enables the light-oil-plant operator to prepare, without further refining, an inhibited benzol that will readily meet all specifications. The substantially complete removal of hydrogen sulfide, carbon disulfide, and low-boiling mercaptans is also accompanied by a similarly complete removal of other compounds in the same boiling range, for example the highly reactive cyclopentadiene and amylenes. The presence of these unsaturates is undesirable in motor benzol and is particularly undesirable in benzol fractions or crude light oils that are to be subsequently refined by acid washing. It has been fairly well established that the amount of sulfur dioxide ("acidity") produced in pure product distillations is roughly proportional to the quantity of cyclopentadiene in the original fraction washed.[19] The improvement in the odor and acidity of pure products prepared at plants equipped with forerunnings strippers has been noted by several authors.[20, 173] There is usually an improvement in the physical properties and emulsion-forming tendency of the acid tars.

In foreign practice, chiefly due to Barbet,[174] the stripping section of the column consists of about 12 plates, while the rectifying section may contain as many as 25 to 30 plates considerably smaller in diameter. In domestic practice, the forerunnings

stripper is usually of the same diameter above and below the feed. Welded sheet steel is used for the shell and tray plates with cast-iron bubble caps bolted to the trays. A construction facilitating ready cleaning is desirable since gummy deposits tend to collect on the trays.[175] Adequately designed water separators are necessary since the presence of two liquid phases on the trays may reduce the fractionating efficiency to but a fraction of its original value. The effectiveness of both domestic and foreign practice may be judged by the fact that values less than 0.005 percent have been reported for the carbon disulfide concentration in the motor-fuel fraction.[20, 176] The quantity of benzol in the forerunnings is substantially zero; the quantity of forerunnings in the bottoms can be held to less than 0.05 percent. In most light oils, the great bulk of the forerunnings is made up of materials boiling below 50° C; there is, however, some evidence to indicate the presence, in the light oil, of a small fraction boiling between 50 and 80° C. By proper manipulation of the column, this fraction can be included in the bottoms, thereby increasing the motor-benzol yield.

Forerunnings strippers are a fairly recent addition to light-oil-refining technique, and it is not surprising that the successful commercial utilization of the product, crude forerunnings, has been slow. Most of the forerunnings now produced are burned as fuel as a constituent of the fuel gas sent to the ovens for underfiring. The recovery of the carbon disulfide present in forerunnings can be accomplished only by chemical means; the low price of the synthetic product has not encouraged the practice. Ward[15] has described a process for the recovery of cyclopentadiene from crude fore-

173 Gillies, A., *Gas World*, **104**, No. 2700, Coking Sect., 52–5 (1936).

174 Soc. des établ. Barbet, Brit. Pat. 441,518 (1935).

175 Dodd, A., *Gas World*, **108**, No. 2809, Coking Sect., 63–72 (1938).

176 Berthelot, C., *Génie civil*, **112**, 141–7 (1938).

runnings as the dimer. The process consists of a polymerization step at 100° C under a pressure sufficient to maintain the liquid phase followed by the removal of the unpolymerized carbon disulfide, isoprene, piperylene, pentenes, pentanes, etc., from the high-boiling dicyclopentadiene by fractional distillation. Cyclopentadiene may also be recovered in the form of addition compounds by treating the forerunnings with *p*-quinone, α-naphthoquinone,[177] and maleic anhydride.[178] Forerunnings may be burned for the manufacture of sulfuric acid. It is claimed that acid washing for thiophene removal is improved in effectiveness by the prior addition of cyclopentadiene-bearing materials to light oil.[27] It is probable that the coexistent amylenes contribute more weightily to this technically useful property of the forerunnings fraction.

At installations carbonizing low-sulfur coals, it is sometimes found that a satisfactory motor fuel of adequately low sulfur content can be prepared by including all the forerunnings fraction in the motor fuel. Naturally, a forerunnings stripper can be dispensed with. However, the carbon disulfide content of forerunnings and the quantity of the forerunnings are markedly affected by changes in coking time and coal mixes. A plant with a light oil of marginal sulfur content may find motor benzol sulfur a problem when the coal mix is varied.

Reverting to Fig. 18, the bottoms from the forerunnings column are fed automatically to the motor-fuel column, the rate of feed being regulated by a float-controlled valve located in the base of the forerunnings column. The motor-fuel system will include a continuous multitray bubble-cap column, a reboiler, a product condenser, a water separator, reflux and feed pumps, flow meters, an automatic base-liquid-level-control, an automatic steam-to-reboiler controller, an inhibitor feeding device, storage tanks, and miscellaneous suitable instrumentation. In construction, the motor-fuel column is in most respects quite similar to the forerunnings stripper, the only important difference being that the trays are fewer.

The feed, substantially a mixture of benzene, toluene, and xylene, is pumped continuously to the proper point in the column, the position of the feed plate depending largely upon the exact analysis of the light oil. The overall effect of the fractionation phenomena taking place in the column is to separate the feed into two portions, the more volatile being removed as vapor from the top, the less volatile being drained as liquid from the bottom. As a simple analogy, the action of a continuous fractionating column may be taken as quite similar to that of a scrubbing or washing column. The liquid bottoms in the reboiler are continuously transformed into a vapor which passes up the column where it meets a liquid flowing downward, in countercurrent stream, the liquid and vapor being in more or less intimate contact with each other, and tending, at any point in the column, to be in thermodynamic equilibrium. The vapor product is condensed and a portion returned to the column to provide the downward-flowing liquid stream or *reflux*. The function of the rectifying section, or that portion above the feed, is to remove the remnants of the less volatile components from the more volatile components in the distillate; the function of the lower or stripping section is to remove the remnants of the more volatile component from the less volatile components leaving the bottom of the column.

177 I. G. Farbenindustrie A.-G., Fr. Pat. 785,-851 (1935).

178 I. G. Farbenindustrie A.-G., Fr. Pat. 785,-852 (1935).

The effectiveness of the separation produced by a column depends upon a large number of factors, among which are: (1) the number of actual bubble-cap trays in each section; (2) the efficiency of the trays, that is, the extent to which the ideal thermodynamic equilibrium conditions are realized; (3) the reflux ratio, expressing the proportion of product withdrawal to product return to the column for scrubbing purposes; (4) the heat losses from the column; and (5) the ease of separation of the components. The last-mentioned variable depends largely upon the form of the vapor-pressure curves of the compounds in the mixture to be fractionated.

Unlike batch distillation, the mathematical treatment of the physical principles involved in continuous distillation problems has been well established. In the application to light oils, the calculations are somewhat more complicated than for binary mixtures, owing to the additional degree of freedom conferred by the addition of each component. Lewis and Matheson [179] have published a workable method. The application of their procedure to a typical light-oil-refining problem has been made by Robinson and Gilliland.[180] These authors considered the rectification of a mixture containing 60 mole percent of benzene, 30 mole percent of toluene, and 10 mole percent of xylene into a product containing not over 0.5 mole percent of toluene and a residue containing not over 0.5 mole percent of benzene. They found that the required separation could be effected, using a reflux ratio of 2, by the use of 16 theoretical plates. For further amplification of distillation theory, the reader is referred to this excellent treatise and to other publications in scientific journals.[181]

Motor-fuel columns may be operated in several ways, the precise mode chosen depending upon the arrangement of piping and the storage-tank facilities, the current market demands for specific products, and the particular philosophy of the operator. If all the benzol fraction is to be sold as motor benzol, the apparatus is adjusted to effect as complete a separation as possible between the benzol and the toluol-xylol fraction. If a certain portion of the total benzol is to be refined to nitration or other pure grades, the column may be operated so that this required amount is retained in the bottom or toluol-xylol cut, whence it is subsequently recovered, after acid treatment, by discontinuous distillation. An alternative procedure is to operate in the manner first mentioned, a portion of the motor fuel being segregated for separate washing in batch equipment. The washed

[179] Lewis, W. K., and Matheson, G. L., *Ind. Eng. Chem.*, **24**, 494–8 (1932).

[180] Robinson, C. S., and Gilliland, E. R., *The Elements of Fractional Distillation*, McGraw-Hill Book Co., New York, 1939, pp. 189 ff.

[181] Brown, G. G., et al., *Trans. Am. Inst. Chem. Engrs.*, **30**, 438–503 (1933–4); *Petroleum Engr.*, **11**, No. 11, 31–4, 36 (1940). Gilliland, E. R., *Ind. Eng. Chem.*, **27**, 260–5 (1935), **32**, 918–20, 1101–6, 1220–3 (1940). Brown, G. G., *Trans. Am. Inst. Chem. Engrs.*, **32**, 321–63 (1936); *Petroleum Engr.*, **11**, No. 9, 55–8, 60 (1940). Colburn, A. P., *Ind. Eng. Chem.*, **28**, 526–30 (1936). Lewis, W. K., *ibid.*, **28**, 399–402 (1936). Othmer, D. F., *ibid.*, **28**, 1435–8 (1936). Edgeworth-Johnstone, R., *Trans. Inst. Chem. Engrs.*, **14**, 107–12 (1936). Kirschbaum, E., and Andrews, C. A., *J. Inst. Petroleum Tech.*, **22**, 803–20 (1936). Strang, L. C., *ibid.*, **22**, 166–76 (1936). Gunness, R. C., *Ind. Eng. Chem.*, **29**, 1092–1100 (1937). Dodge, B. F., and Huffman, J. R., *ibid.*, **29**, 1434–6 (1937). Meyer, P., *Trans. Inst. Chem. Engrs.*, **15**, 209–22 (1937). Siegel, C. L., *Chem. & Met. Eng.*, **44**, 493–7 (1937). Keyes, D. B., *Univ. Illinois Eng. Expt. Sta., Circ.* **35**, 3–14 (1938). Randall, M., and Longtin, B., *Ind. Eng. Chem.*, **30**, 1063–7, 1188–92, 1311–5 (1938), **32**, 125–9 (1940). Webber, H. A., and Bridger, G. L., *ibid.*, **30**, 315–8 (1938). Jenny, F. J., *Trans. Am. Inst. Chem. Engrs.*, **35**, 635–77 (1939). Carey, J. S., *Chem. & Met. Eng.*, **46**, 314–7, 336 (1939). Hibshman, H. J., *Ind. Eng. Chem.*, **32**, 988–91 (1940). Smith, R. L., *Trans. Am. Inst. Chem. Engrs.*, **37**, 333–61 (1941)

motor fuel may be accumulated and run through the motor-fuel column in a continuous way. Some difficulty may be encountered in washing crude benzol fractions effectively. This seems to be due in part to the fact that only small amounts of heat are developed. There is also considerable evidence to indicate that the styrene and indene usually found in crude secondary light oils and toluol-xylols have a beneficial effect on the efficiency of acid washing. Crude benzols can be successfully washed if the batch charge is preheated in a suitable manner. The addition of a small amount of crude solvent should also be a useful technique.

In the inhibitor process, the only further treatment necessary to the production of specification motor fuel consists in the addition of small amounts, 0.002 to 0.006 percent, of an appropriate organic antioxidant. This is conveniently introduced continuously into the motor fuel as it flows to the storage tanks.

The inhibitor process is probably the most outstanding of the various mild refining processes that have been developed in an attempt to avoid the large loss of unsaturates entailed in the older conventional sulfuric acid treatment. Hoffert and others [182] made the observation that the formation of gum from the unsaturates present in unwashed benzol took place through an initial oxidation step and that the addition of very small amounts of antioxidants would effectively forestall gum development. The effect of the inhibitor is to prevent oxidation almost entirely for a limited period, the *induction period*. In time, the inhibitor is destroyed and gum formation proceeds in the normal way. It is not difficult to obtain induction times of a year

or more by the use of remarkably small amounts of antioxidant. The length of the induction period is approximately proportional to the concentration of added inhibitor; the *optimum* concentration depends upon the particular nature of the crude, the nature of the containing vessel, and the temperature and desired time of storage. The inhibitor itself frequently contributes to the color and residue of motor benzols; hence as little is added as is necessary to prevent gum development before use of the fuel.

Although a very large number of compounds have been patented as inhibitors,[183] most of the effective members can be found in the class of mono-, di-, and trihydric phenols, amino compounds, aminophenols, nitro compounds, and pyridine. Of these, the most efficacious, from the standpoint of inhibiting power per unit and resistance to water, is the class of the substituted aminophenols. Monobenzyl-para-aminophenol, isobutyl-para-aminophenol, and *n*-butyl-para-aminophenol are all vigorous inhibitors and have been widely used in American practice. Mixed inhibitors are also used; for example, one inhibitor now commercially available is composed of substantially equal parts of isobutyl-para-aminophenol and the xylenols.

Although inhibited motor fuels, when freshly produced, may fail to meet visible color specifications, it has been observed that the color fades to a satisfactory value on two or three days' storage. In obstinate cases of unsatisfactory color, a light sulfuric acid wash may be necessary. The inhibitor process is frequently combined, especially in foreign practice, with some degree of mild chemical refining.[26, 184] The

182 Somerville, P. G., and Hoffert, W. H., Brit. Pat. 289,347 (1926). Hoffert, W. H., U. S. Pat. 1,816,811 (1931).

183 Byers, J. H., *Natl. Petroleum News*, **29**, No. 11, 157–60, No. 15, 58–61 (1937).

184 Hoffert, W. H., and Claxton, G., *Fuel*, **9**, 440–7, 476–81 (1930) ; *J. Soc. Chem. Ind.*, **52**, 25–33T (1933) ; *J. usines gaz*, **57**, 178–82, 208–

use of inhibited benzols for blending purposes poses no problem to the petroleum fuel manufacturer since fully half of the gasoline sold today, and all cracked distillates, are inhibited. As a result, most of the recent contributions to inhibitor technology have come from the workers in the petroleum industry.[185]

Returning to Fig. 18, the hot toluol-xylol bottoms, which may or may not contain some crude benzol, are run out, through a cooler, to a storage tank. The cooler can be arranged as a heat exchanger, the cooling agent being the feed to the column. The production of this crude toluol-xylol represents the end of the continuous portion of the semi-continuous plant; all further operations are carried out in a batch way.

Although a large number of processes have been devised for the refining of motor fuel, no significant advance, since Mansfield,[172] has been made in the chemical refining of light-oil constituents for the preparation of pure products. The treatment always involves washing strongly with sulfuric acid and caustic, followed by redistillation. Although various continuous processes of chemical treatment have been introduced from time to time, the batch acid wash agitator is still the favorite type of apparatus.

The conventional agitator consists of a cylindrical tank, of 5,000- to 13,000-gallon

capacity, fitted with a conical bottom and provided with appropriate inlet piping, sludge drain piping, a suitable cover, and a means of agitation. All parts of the apparatus that come in contact with the acid may be heavily lined with lead sheet although the use of unprotected steel is more common. The agitation is usually furnished by a centrally located vertical shaft bearing impellers or centrifugal pumps so designed that an intimate contact is effected between the heterogeneous system of acid and oil phases. Another method involves the use of propeller mixers on horizontal shafts, introduced tangentially through the wall of the lower part of the cylindrical body of the agitator. Some means of cooling the reaction mixture is desirable, such as either an external water jacket or a set of internal coils. Usually, however, no cooling equipment is provided.

A typical procedure involves charging with the crude light oil, crude benzol, crude toluol-xylol, or any appropriate fraction, followed by the slow introduction of strong sulfuric acid (66° Baumé). The acid is commonly added in several portions, each addition being followed by suitable agitation, settling, and withdrawal of the sludge. The first stage is frequently a dehydration treatment in which an acid quantity equivalent to about 0.33 percent of the oil volume is used. In this way, a saving is made in the total amount of acid consumed. Usually, considerable heat is developed, and some means of cooling would result in a saving of time. The total amount of acid necessary, the number of portions in which it is added, and the time allowed for agitation and settling are all dependent upon the particular nature of the crude and are chiefly established by experience and tradition. The extent to which removal of the unsaturates has occurred can be followed by analytical means. When acid washing

11 (1933); *Gas- u. Wasserfach*, **76**, 704–10 (1933). Voorhees, V., *Oil Gas J.*, **34**, No. 30, 36, 39, 41–2 (1936).

185 Egloff, G., Morrell, J. C., Lowry, C. D., Jr., and Dryer, C. G., *Ind. Eng. Chem.*, **24**, 1375–82 (1932), **25**, 804–8 (1933), **26**, 497–503, 655–8, 885–8 (1934), **27**, 15–20, 315–7, 413–5 (1935); *Oil Gas J.*, **31**, No. 45, 64 (1933), **33**, No. 12, 8 (1934). Dryer, C. G., Morrell, J. C., and Egloff, G., *ibid.*, **35**, No. 45, 113–4 (1937). Lowry, C. D., Jr., *Trans. Electrochem. Soc.*, **69**, 186–93 (1936). Lowry, C. D., Jr., Dryer, C. G., Wirth, C., III, and Sutherland, R. E., *Ind. Eng. Chem.*, **30**, 1275–9 (1938).

is complete, the agitator contents are neutralized by washing with aqueous caustic soda, again in several stages followed by intermediate settling. Although aqueous caustic soda is the normal neutralizing agent other materials like lime, ammonia, and carbonates (phenol purification system) may be used. Spent caustic soda from vapor neutralizers is often employed in preliminary washes. When using carbonates it is usually necessary to finish with a final caustic soda treatment. Water washes before neutralization are frequently made, with or without agitation, depending upon the emulsifying tendency of the oil. The treatment of a batch requires from 5 to 8 hours, this elapsed time again depending upon the nature of the oil, the specifications of the refined products, and the artifices which may be practiced to obtain economy in reagent consumption at the expense of time of treatment. In general, the shrinkage loss in washing a typical crude light oil is from 4 to 6 percent by volume; the acid consumed is 0.40 pound of 66° Baumé per gallon of oil; and the caustic consumption will average 0.06 to 0.12 pound of sodium hydroxide per gallon of oil. The losses involved in washing particularly unsaturated fractions such as the crude toluol-xylol or solvent cuts may be very much higher than these mean values.

The reactions occurring in the acid-washing step [24] are many and complicated but include the following: (1) sulfur compounds are dissolved or oxidized; (2) nitrogen bases (pyridine, etc.) and some unsaturates combine with the acid; (3) unsaturates are polymerized; (4) aromatic compounds are sulfonated; (5) some aromatics condense with particular unsaturates; and (6) some unstable hydrocarbons are oxidized. The optimum conditions are those in which the desired removal of unsaturates, thiophene, pyridine, etc., is accomplished with an accompanying minimum sulfonation of the aromatic hydrocarbons and a minimum consumption of reagent acid and caustic.

The acid sludge drained from the agitator during the washing process is an intimate mixture of unused acid, entrained light oil, and reaction products: "resins." In modern practice, this material is usually taken to some convenient spot and burned. In the past, fairly elaborate acid reclaiming plants have been devised and built; in general the value of the reclaimed materials failed to justify the labor, maintenance, and investment costs of the reclamation equipment. A few of these plants can still be found at American installations. In foreign technology, sludge recovery plants are more common. Designs fall into two categories: (1) processes involving dilution of the acid sludge with water or with solutions of alkali, ammonia, ammonium sulfate, etc., in water; and (2) procedures in which a stream of hot gases or direct steam is passed into the heated sludge and the distillates recovered. Many processes have been described in the literature.[186]

186 Chemische Fabrik A.-G., Ger. Pats. 34,947, 36,372 (1886). Roelofsen, J. A., and Shuttleworth, L., Brit. Pat. 260,514 (1926). Stolzenwald, G., Ger. Pats. 212,000, 213,589 (1909). Gasser, A., Ger. Pat. 272,130 (1914). Phoenix A.-G., Ger. Pats. 289,162 (1915), 289,524 (1916), 299,073 (1920). Hilpert, S., Ger. Pat. 319,011 (1920). Schümmer, J., Ger. Pat. 320,255 (1920). Stephenson, G., Gas World, 74, No. 1907, Coking Sect., 19–20 (1921); Chem. Trade J., 68, 176 (1921). Koholyt A.-G., Ger. Pat. 403,647 (1921). Benesch, E., Ger. Pat. 388,467 (1922). Still, C., Brit. Pats. 219,089 (1923), 277,619, 281,547 (1927); U. S. Pat. 1,835,941 (1931). Laube & Menzen Tech. Büro, Ger. Pats. 372,108, 381,503, 385,644 (1923). Kattwinkel, R., Ger. Pat. 395,597 (1924). Menzen, H., Ger. Pat. 426,387 (1924). Schlamp, H., Chem. & Met. Eng., 30, 188 (1924). Demann, W., Ger. Pat. 430,242 (1925). Kugel, E., Schwenke, H., Ger. Pat. 454,307 (1928). Conklin, E. B., U. S. Pat. 1,855,878 (1932). Bartholomew, F. J., Chem. & Met. Eng., 40, 642–5 (1933). Ruys, J. D., U. S. Pat. 2,022,813 (1935). Pyzel, F. M.,

Although most acid washing is carried out in a batch way, a few continuous-type installations exist. One typical example,[187] as built by the Koppers Company, is shown in Fig. 20. Essentially, this interpretation of the continuous process involves simply the provision of an interconnected row of tanks for the various operations of treating with acid, settling, neutralizing, and again settling. The incorporation of an additional tank for agitating the sulfuric acid-oil mixture with water allows the recovery of dilute acid free from resins.

Continuous processes have been devised utilizing continuous centrifuges for the separation of the oil and sludge.[188] One difficulty lies in the fact that the techniques are not uniformly successful on all light oils. Separation of the oil and sludge is accomplished, at one foreign installation, by filtration through a quartz filter.[189]

The various models of batch agitators show few essential differences. The archetypal, cylindrical, conical-bottom, sometimes lead-lined, steel shell is eminently persistent; most of the designers' variations are confined to modifications of the standard, top-driven, vertically supported means of agitation. Somewhat more radical in departure are the constructions of Pfisterer and Eming and Kesper.[190] Pfisterer devised a mixing device based on the injector principle; Eming and Kesper described an agitator constructed in the form of one large cylinder superimposed upon a some-what smaller one. The sulfuric acid collects in the lower cylinder; the benzene or light oil in the upper compartment is pumped down into the sulfuric acid, through which it is forced in many finely divided streams. A structure of baffles in the lower part of the upper tank facilitates the ready separation of light oil and spent wash reagent.

A refining technique consisting of stirring a material with sulfuric acid possesses the advantages of simplicity and cheapness and is difficult to improve. Little can be said for more complex procedures. The chief disadvantages of the unornamented process as now practiced are: (1) a lack of complete selectivity accompanied by some sulfonation of aromatic hydrocarbons; and (2) the formation of an economically useless sludge. Most of the modifications are directed, usually unsuccessfully, to the elimination of one or the other.

Gluud and Schneider [191] recommended a preliminary wash with a small quantity of 35 percent sulfuric acid followed by settling and draining. Pyridine and pyridine homologs were thus recovered as the sulfates. The preliminary weak wash may again be followed by a weak caustic wash for the recovery of phenols, etc. Pieters and Mannens [192] reported yields of about 2 kilograms of pyridine and 3 kilograms of phenol per metric ton (1,000 kilograms) of oil, using this procedure. Demant [193] improved the selectivity of the treatment by using relatively weak acids (46 to 48° Baumé) at elevated temperatures. Jaeger [194] found that a mixture of sulfuric

and Ruys, J. D., U. S. Pat. 2,026,250 (1935). Scott, A. T., U. S. Pat. 2,155,367 (1939). Carr, W. F., Woolhouse, T. G., and Green, W., Brit. Pat. 501,077 (1939).

[187] Kemper, A., U. S. Pat. 1,942,062 (1934).

[188] Aktiebolaget Separator-Nobel, Ger. Pat. 581,584 (1933) ; Fr. Pat. 785,078 (1935).

[189] Lelli, C., *Industria chimica*, **7**, 152–6 (1932).

[190] Pfisterer, K., Brit. Pat. 232,730 (1924). Eming, K., and Kesper, J. F., *Chem. App.*, **22**, 58–9 (1935) ; *Teer u. Bitumen*, **33**, 64–6 (1935).

[191] Gluud, W., and Schneider, G., *Ber. Ges. Kohlentech.*, **1921**, (2) 93–111; *Glückauf*, **22**, 464 (1922).

[192] Pieters, H. A. J., and Mannens, M. J., *Chem. Weekblad*, **26**, 286–90 (1929).

[193] Demant, J., Brit. Pat. 179,610 (1921).

[194] Jaeger, A. O., U. S. Pats. 1,674,472 (1928), 1,729,543 (1929).

acid and a halogenating agent was desirable, the amount of the sulfuric acid being insufficient to carry out the ordinary acid-washing reactions. Albright [195] followed the acid wash by a treatment with the aqueous sodium phenoxide obtained in the dephenolization of gas liquor. Ott [196] used a mixture of sulfuric acid and phenolic water or aqueous emulsions of phenolic oils. A preliminary wash with weak used acid, followed by the customary strong sulfuric acid wash, has been patented by Still.[197] An improvement in thiophene removal may be effected by the admixture of phosphoric acid.[198] Nettlenbush and Schneider [199] believed that emulsion troubles could be reduced by the addition of naphthalene to the light oil before acid washing and by carrying out the neutralization step at an elevated temperature. Potolovskiĭ and Atal'yan [200] found that the yields of pure product, benzol, toluol, and xylol, were greatly improved by a combined treatment with aluminum chloride and sulfuric acid. Gould [201] has patented a process featuring replacing the customary neutralization step by neutralization of the distillates.

Of somewhat more interest, because of its use at several installations in this country, is the modification of the acid-washing treatment known as the Ufer process.[202] This procedure provides a simple means for the regeneration, *in situ*, of the acid

sludge. The light oil is first washed in the usual way by agitation with sulfuric acid of a rather critical strength. The acid tars are not removed; instead, as soon as the reaction is complete, a measured amount of water is added to the contents of the agitator. If all the variables are properly controlled, the acid will separate from the "resins," and the resins, in most part, will enter into solution in the light oil. The separated weak acid (39 to 40° Baumé) can be utilized at the ammonium sulfate recovery plant with no further treatment. Successful operation of this process depends largely upon the nature of the light oil; with some raw stocks, the process may fail owing to the precipitation of a hard pitch difficultly soluble in the oil layer. With other oils, only partial success may be enjoyed, a certain amount of nonsoluble sludge being formed and withdrawn in the usual way. Where the process is applicable, it is found that uniformity of success can be ensured by a careful control of temperature and acid concentration accompanied by very thorough agitation.

Page [203] has described a practical time schedule for the Ufer process as practiced at the Montreal Coke and Manufacturing Company. He noted that, although the use of Ufer acid in the ammonia-recovery saturators had no deleterious effect on the color of the ammonium sulfate, there was a definite tendency towards the formation of fine crystals. Phillips [204] reported that the particular advantages of the Ufer process made the system especially adaptable to the continuous method of washing; the procedure, of course, is very readily applicable in batch equipment. The advantages of the Ufer process, as claimed by the pro-

195 Albright, A. R., Brit. Pat. 335,155 (1929).

196 Ott, A., Ger. Pat. 574,805 (1933).

197 Still, C., Fr. Pat. 803,038 (1936).

198 Hahn, C. A., and Nielsen, H., Dan. Pat. 51,230 (1936).

199 Nettlenbush, L., and Schneider, R., Ger. Pat. 640,736 (1937).

200 Potolovskiĭ, L. A., and Atal'yan, A., *Azerbaĭdzhanskoe Neftyanoe Khoz.*, 1939, No. 10/11, 55–60.

201 Gould, D. F., U. S. Pat. 2,185,406 (1940).

202 Ufer, A., Brit. Pat. 251,117 (1926); Ger. Pat. 489,758 (1930). Rosendahl, F., *Petroleum Z.*, 27, 937–8 (1931). Freitag, *Chem.-tech. Rundschau*, 46, 490–1 (1931). Krebs, O., *Chem.-Ztg.*, 56, 509–11, 531–2 (1932).

203 Page, G. W., *Gas J.*, 211, 565–6 (1935).

204 Phillips, O. B., paper presented at the meeting of the Blast Furnace and Coke-Oven Association of the Chicago District, Joliet, Ill., June 3, 1931.

ponents of that method, may be summarized as follows:

1. Practically all (90 percent) of the acid not consumed in the acid-washing reactions is recovered in a state suitable for use without further treatment in the ammonia saturators of the byproduct plant.

2. In most cases, no permanent sludge is formed or remains to be disposed of as such; the resins dissolved in the light oil are recovered on distillation and may be added to the tar.

3. The consumption of alkali is reduced.

4. Light-oil losses, both by acid reactions and mechanical losses in the sludge, are reduced.

Returning to Fig. 18, the agitator charge, or an accumulation of agitator charges, is pumped to the still kettle of the batch still (pure products) system. The essential apparatus comprises, in addition to the kettle, a bubble-cap tray still column, a vapor neutralizer with accessories, a vapor condenser, an arrangement of appropriate receivers, and a reflux pump. Instrumentation should include the automatic recording of temperatures on chosen trays in the column and suitable means of measuring product and reflux flows.

The batch rectifying column has a functional construction almost identical with that of the continuous columns. It is obviously possible to dispense with any still tank and automatic-base-liquid-level control; the liquid draining from the lowest tray may be returned directly to the still kettle. Indirect moderate-pressure steam ordinarily furnishes the necessary heat energy for vaporization, although other fluids, like Dowtherm, may be employed. The heating coils are usually arranged to allow for convenient removal in integral units since frequent cleaning may be desirable.

The vapor neutralizer is a device, consisting of perhaps two bubble-cap trays

fed with an aqueous caustic soda solution, which serves to scrub any acidic constituents from the hydrocarbon vapors before condensation. The acid constituents, hydrogen sulfide, sulfur dioxide, and free sulfur, are responsible for "corrosive" products, a familiar bugbear to many refiners. Although hydrogen sulfide and sulfur dioxide may be removed by cold caustic washing in the liquid phase, free sulfur resists such treatment. In the vapor neutralizer the distillate, in the gas phase, comes into intimate contact with a hot caustic solution; this drastic treatment results in the complete removal of all acidic constituents and free sulfur. The concentration of the aqueous alkaline solution is adjusted so that the boiling point is at least not below the temperature of the vapors. The apparatus is usually well insulated, and supplementary heating coils on the trays are not necessary. Fouled caustic solutions may be reused, at least as preliminary washing agents, in the acid-washing treatment.

After neutralization, the vapors are condensed in apparatus of the drip type previously described, the condensate flowing to gravity separators where any nondissolved water that may be present is removed. A portion of the product is returned as reflux, the balance passing to various receivers. Although the vapor temperature is an important and valuable guide, it is usually customary to perform a control analysis on the contents of each receiver; such control analytical work is frequently restricted to a determination of the boiling range in standardized single-bulb distillation apparatus.

Since the charge is ordinarily a mixture of benzene, toluene, xylene, solvent, and the small amounts of impurities associated in boiling point with these hydrocarbons, the product composition and the rate of change of product composition will vary *continuously* throughout a distillation. At first,

assuming the prior removal of forerunnings, a relatively large amount of benzol is obtained, the quality depending upon the nature of the charge, the performance characteristics of the column, and the particular techniques of reflux ratio and rate of boil-up employed. This benzol cut will be continuously variable in quality as the distillation progresses and will ordinarily be diverted to suitable storage tanks as 1° Benzol, 2° Benzol, etc. As the amount of benzol in the kettle charge and in the column becomes smaller, appreciable quantities of the next-higher-boiling material, toluene, will appear in the product. The concentration of toluene rapidly becomes larger, eventually reaching a value such that the nature of the product coincides with the specifications of one of the grades of toluol the refiner is attempting to prepare. The material collected between the last usable grade of benzol and the first usable grade of toluol is referred to as an "intermediate"; its size, expressed in percentage of the still charge, depends upon the refiner's topical definitions of usable benzol and toluol, the nature of the charge, the efficiency of the still, and, most significantly, the mode of still operation employed with respect to reflux ratio and boil-up. The intermediates are not immediately useful and must be refractionated to recover the benzene and toluene they contain. The same phenomena reoccur as the toluene is gradually removed and the nature of the product approaches continuously to that of a usable xylol; the phenomena are again reproduced as the washed solvent is obtained; finally only a nondistillable residue ("pure still residues") remains.

All other things being equal, the relative effectiveness of batch stills may be evaluated in terms of the amounts, expressed in percentages of the charge, of directly nonusable intermediates.

Considerable controversy exists over the apparently simple question of how to operate light-oil batch stills. One group finds it desirable to greatly increase the reflux ratio as the "cut-over" point between the homologs is approached, even going so far as to operate for short periods at total reflux. In the "sweating-off" procedure, it is undeniably true that the percentage length of intermediate is decreased. Another school operates distillation throughout at a relatively low reflux ratio with the correlative collection of rather large intermediates followed by a similar treatment or rerunning of these large intermediates. A suitably convincing theoretical treatment has not yet been established for discontinuous distillation; hence, the proper choice cannot be made from considerations of physical chemistry alone. Fortunately, for any given still, a decision can be based on costs, since, by operating in either way, the same desired ultimate yields can be obtained. With stills of modern design, the sweating-off method of operation has been found undesirable inasmuch as it leads to higher distillation refining costs per unit of product. Although many factors such as labor costs and investment costs contribute to the final value, the charge for heat energy for boil-up is most significant. The reduction in the length of the intermediate produced in the sweating-off procedure is accompanied by an economically inordinate consumption of steam.

The physical theory of continuous fractionation has long been adequately established; the historically older batch fractionation has been comparatively neglected. Writers on distillation have been prone to dismiss the subject with such statements as, "All the methods of calculation described (for continuous distillation) can obviously

be applied to discontinuous distillation." The misleading character of such remarks is obvious to anyone who has attempted to solve the differential equations involved. In continuous fractionation, the necessary theory need only describe a steady-state system; in discontinuous fractionation, conditions are continuously changing with time, and a steady state never exists. Further, in continuous fractionation some characteristics of the system such as the internal and external hold-up have no appreciable effect on the result, whereas the same variables profoundly influence the course of batch distillation and introduce a corresponding complexity into the mathematical treatment.

Much of the void has been filled by an excellent series of papers due, in large part, to Rose, Smoker, and their associates. These workers have adequately investigated the effects of varying reflux ratios and operating hold-up for certain special conditions of operation.[205]

Light-oil batch still operators are generally interested in operation at a reasonably low reflux ratio with a column having a fairly large internal hold-up, which still lacks an adequate theoretical discussion. The experience and data obtained with small-scale laboratory stills cannot be extrapolated with any validity to industrial-scale installations. In an attempt to obtain more utilizable information, Colburn and Stearns have investigated, experimentally, the effect of column hold-up in a 7-

inch, 15-plate column.[206] A most significant and unexpected result was their observation of the *beneficial effect*, under certain conditions, of the presence of appreciable column hold-up; the separation actually obtained was always sharper than that theoretically predicted for zero hold-up. Equally striking was the combined effect of hold-up and reflux ratio; for a certain range of values of the hold-up, the separation actually achieved was substantially independent of reflux ratio. The beneficial effect of hold-up was greater at the lower reflux ratios, an observation, if confirmed, of profound importance to the designers of batch light-oil fractionating columns. The owner of an industrial fractionating column cannot readily change the actual hold-up of the plates; the same effect, however, can be easily obtained by simply varying the still-kettle charge.

The pure still residues, somewhat high in sulfur,[207] are usually burned as fuel. Volatile resin oils can be recovered by steam distillation [146] of the residue, leaving a brittle resin. The resin oils have been examined by Carmody and Kelly,[208] who found a family of pseudopolymers composed generally of one molecule of the ordinary aromatic homologs combined with one molecule of an unsaturated aromatic of the type indene, coumarone, dicyclopentadiene, styrene, cyclopentadiene, etc. Carmody [209] has patented processes involving heating the residues to 200 to 275° C and blowing with live steam to obtain a volatile oil. The distillate may be further subjected to catalytic cracking with aluminum

205 Bogart, M. J. P., *Trans. Am. Inst. Chem. Engrs.*, **33**, 139–52 (1937). Smoker, E. H., and Rose, A., *ibid.*, **36**, 285–93 (1940). Rose, A., Welshans, L. M., and Long, H. H., *Ind. Eng. Chem.*, **32**, 673-5 (1940). Rose, A., and Welshans, L. M., *ibid.*, **32**, 668–72 (1940). Rose, A., *J. Am. Chem. Soc.*, **62**, 793–5 (1940); *Ind. Eng. Chem.*, **32**, 675–6 (1940), **33**, 594–7 (1941). Rose, A., and Long, H. H., *ibid.*, **33**, 684–7 (1941).

206 Colburn, A. P., and Stearns, R. F., *Trans. Am. Inst. Chem. Engrs.*, **37**, 291–309 (1941).
207 Wehrmann, F., *Gas- u. Wasserfach*, **68**, 658–9 (1925).
208 Carmody, W. H., and Kelly, H. E., *Ind. Eng. Chem.*, **32**, 954–7 (1940).
209 Carmody, W. H., U. S. Pats. 2,143,474, 2,149,577 (1939), 2,210,895 (1940).

chloride to yield a resin and the primitive aromatic.

The pure batch still distillates benzol, toluol, xylol, and solvent naphtha, in various standard grades, are usually dehydrated before shipment. This may be readily accomplished by percolation through beds of activated alumina, calcium chloride, or caustic soda.[210]

Occasionally the pure products, particularly toluols and xylols, may be characterized by unpleasant odors. Deodorization can often be effected by agitation with an aqueous solution of sodium hypochlorite or by treatment with chlorine, bromine, iodine, or mercuric chloride. The addition of perfume is an insidious artifice that has, fortunately, had only a limited use.

It will be noted from the above that the usual light-oil-refining process is restricted to a combination of sulfuric acid washing and fractional distillation. Relatively inert impurities having boiling points close to those of the aromatic homologs elude such a scheme and, if present in the stock, tend to pass unchanged into the various products. This is particularly true of "paraffins," and the preparation of specification grades of nitration benzol and toluol becomes increasingly difficult as the concentration of paraffins in the stock increases, perhaps as a result of long carbonization times and correspondingly lower oven temperatures. The successful utilization of high-paraffin stocks requires the development of new, more powerful refining techniques.

The separation of hydrocarbons from impurities of nearly the same boiling point by application of third component or azeotropic distillation has been described for the important toluene-paraffins [29, 211] and

is the subject of several patents.[212] A successful azeotropic process for the treatment of high-paraffin toluene is used in England.[213]

The removal of paraffins from benzol, a simpler problem, can be readily accomplished by crystallization,[214] the nonaromatic impurities tending to concentrate in the mother liquor. In current American practice, the design is based on standard ice-making machinery and ordinarily operates in a batch way. One Pittsburgh plant consists of a suitably arranged series of 112 ice "cans," each can measuring 10⅞ by 22 by 49 inches. Benzol is charged to the cans to a depth of 40 inches and then gradually frozen over a period of 38 hours, heat being withdrawn by circulated brine. Throughout the freezing step a small stream of air introduced through the bottom of the can flows as a stream of bubbles up through the unfrozen core. About 85 percent of the charge is frozen. At the end of the freezing step the core material is drained away and the frozen purified benzol is thawed by the circulation, for a period of 8 hours, of warm water through the brine coils.

THE CONTINUOUS PLANT

Installations of continuous light-oil-refining plants are rare in American practice. The particular advantages inherent to operation in a continuous manner are, for small and moderate-sized units, overbalanced by the complexity and costliness of the equipment; here, the semi-continuous plant offers a reasonable compromise. The

210 Klemstedt, H., *Brennstoff-Chem.*, **18**, 23–4 (1937).

211 Mizuta, M., *J. Soc. Chem. Ind. Japan*, **35**, 470B (1982).

212 Roelfsema, P. J., Fr. Pat. 804,488 (1936); U. S. Pats. 2,069,329, 2,085,546 (1937), 2,113,965 (1938); Brit. Pats. 462,630, 464,307 (1937). Haltermann, J., Fr. Pat. 831,295 (1938).

213 Woodall-Duckham, Ltd., *Gas World*, **111**, No. 2888, suppl. page xiii (1939); Brit. Pat. 536,172 (1941). *Gas World*, **112**, 279 (1940).

214 Campbell, R. W., and Wagner, F. W., U. S. Pat. 1,991,844 (1935).

profitable exploitation of the continuous principle requires very large capacities; it is noteworthy that this system has been recently applied in the modernization of the largest light-oil plant in the world, that of the Carnegie-Illinois Steel Corporation at Clairton, Pa.[215] The plant, Fig. 19, consists of eight stills arranged in two sections of three "crude" and five "pure" stills.

In general, the method of operation consists of first recovering the light oil from the absorbent medium as one fraction by use of the conventional-type steam-stripping still; that is, no rectifier is employed. In the crude-still section of the plant, the crude light oil thus obtained is separated by continuous fractional distillation to produce as individual distillates: (1) a forerunnings cut; (2) a crude benzol cut; (3) a broad fraction containing benzol, toluol, and xylol; and (4) a residue cut consisting of higher-boiling solvents, wash oil, and naphthalene. The residue cut is *batch*-distilled for the recovery of high-boiling solvents; the crude benzol-toluol-xylol cut is washed with sulfuric acid in the normal way and, when thus treated, becomes the feed to the pure-still section of the continuous distillation plant. In this plant, an arrangement of five stills, the acid-treated mixture is separated into the ordinary major components of light oil: commercially pure grades of benzol, toluol, xylol, and solvents. Thus eight stills, in this system, perform the functions of the three stills necessary in the semi-continuous plant. However, the continuous rectifier of the debenzolization plant has been omitted.

The detailed mode of procedure is well shown in the flow diagram, Fig. 19. The crude light-oil stock is pumped continuously at a feed rate of 5,000 to 6,000 gallons per hour and enters at approximately the middle of unit 1. In unit 1 the feed is divided into a top distillate of forerunnings and a bottoms fraction of topped light oil. The light distillate is revolatilized into the fuel-gas lines; the bottom product is transferred directly to the fractionating column of unit 2. In unit 2 the separation is arranged so that the top product represents only a portion of the crude benzol and is utilized for the manufacture of inhibited motor fuel; the discharge from the base of the column contains all the toluol, xylol, and higher-boiling materials originally present in the light oil plus the quantity of benzol needed for the preparation of washed or pure grades. Unit 3, again fed by pumping from the reboiler of unit 2, serves to remove the heavy solvents from the feed; the top product is essentially a mixture of only crude benzol, toluol, and xylol. The separation problem in unit 3 is relatively easy, and the column is fitted with fewer trays than the columns of units 1 and 2. This third still performs the function of the light-oil rectifier usually included in the flow diagram of a modern debenzolization plant. The residue from unit 3 is accumulated and worked up in a batch still; the overhead product is run to storage tanks for subsequent sulfuric acid treatment. This last step represents a discontinuity in the system considered as a whole, since the acid washing is carried out in the ordinary batch way.

Piping has been provided so that various combinations of the three crude units are possible. Thus, the first unit can be operated to produce an overhead containing all the forerunnings plus the benzol; in this event the second unit will effect the separation of forerunnings from the benzol, the forerunnings being obtained as an overhead product and the crude benzol as a side stream near the base of the fractionating

FIG. 19. Flow diagram of the continuous light-oil-refining plant of the Carnegie-Illinois Steel Corporation at Clairton, Pa.

column. In this procedure, the bottoms from unit 1 serve as the feed to unit 3, which performs the same function as before. As another alternative, if all the benzene is to be resolved to pure products, the second still serves no purpose and can be completely bypassed. The first unit then is again operated as a forerunning stripper, the residue or bottom product being pumped directly to unit 3.

In the pure section, the feed, an acid-washed mixture of benzol, toluol, and xylol, is introduced near the top of unit 5. The only separation effected here is the removal of nonvolatile polymerized residues from the overall benzol-toluol-xylol mixture. The top distillate is transferred to one of three 35,000-gallon tanks.

The purpose of these tanks is to serve as surge take-up and at the same time maintain sufficient storage of materials to insure a uniform feed to the succeeding pure product units. Since the remaining units from this point are continuous in operation, in that the residue from each reboiler is used as feed to its successor, and since the uniform balance of product removal in relation to feed must remain in constant equilibrium, in order to obtain maximum product quality, it can be seen that uniform feed to unit is of utmost importance.[215]

Provision has been made for the direct utilization of the distillate from unit 4 as the feed to unit 5, thereby bypassing the tanks mentioned above. This mode of operation is undesirable and is resorted to only in dire necessity.

The quality of product which is recovered from number five still will, of course, depend upon the character of the light oil; and the function of this column is to remove the low-boiling constituents from the washed benzol-toluol-xylol fraction prior to the production of pure benzol in column six. It has been found that this product is free from corrosion as indicated by the copper strip method.

The product from the reboiler of this unit is transferred directly into the column of unit number six, the function of which is the production of high-quality pure benzol. The unit has been found capable of producing a product with a boiling range of less than 1° C without difficulty in addition to a high freezing point. The benzol is neutral in reaction, the corrosion test negative, and the wash test has been found to be equivalent to Barrett number one or less.

The material which collects in the reboiler will obviously contain all of the toluol, xylol and higher-boiling homologs [the latter presumably present due to the inadequacy of unit 3] together with a small amount of benzol and intermediate fractions. The purpose of the following unit, therefore, is to remove the intermediate material which boils between the benzol and toluol fractions in order to provide for the recovery of toluol of high purity in the next succeeding unit. It can readily be seen that the character of the distillate from unit number seven will be subject to considerable fluctuation in the boiling range and may vary between 10 and 30 degrees, depending upon the character of the benzol desired from the previous column as well as the toluol desired from unit number eight. This number seven unit, therefore, is for the removal of the intermediate fraction, and this is accomplished in the same manner as has been described for unit six in that the material is fed into the unit near the center of the column and the intermediate product recovered as a distillate.

The material from the reboiler of this unit number seven, which consists of toluol, xylol, etc., is transferred to unit eight for the removal of commercially pure toluol as a distillate and a xylol fraction as a side cut, while the material in the reboiler will consist of part of the xylol fraction in addition to higher-boiling solvents.

The quality of toluol which has been produced has been found to have less than 1° boiling range, is neutral in reaction, free from corrosion, and has a low Barrett wash test.[215]

It seems reasonable to expect that the production of xylol as a side stream taken off below the feed plate would not allow the preparation of a narrow-range material and that the resultant xylol would be con-

taminated with any nonvolatile constituent of the feed. In order to provide additional flexibility for the manufacture of special products, a battery of five batch stills is operated in conjunction with the continuous units. Each continuous unit consists of a reboiler or base heater and a bubble-cap rectifying column which is connected to condensers, product coolers, decanters, and pump tanks. The pump tanks in the pure unit are sometimes supplemented by small individual product receivers.

The reboilers consist of cylindrical tanks placed at yard level and so arranged that the longitudinal centerlines are horizontal and parallel. At those units where the bottom product is to be transferred as the feed to a succeeding fractionating tower, the reboiler is divided into two sections by a solid partition wall, the two compartments being interconnected through an external pipe-line at the base and vent lines at the top. One compartment contains all the heating elements and serves as a reboiler proper; the other section is used as a surge or reservoir tank. The heating sections are designed for ready removal. Each reboiler section is provided with a separate steam supply, the rate of steam admission, hence the amount of boil-up, being controlled by devices sensitive to the developed pressure in the vapor space. The rate of bottoms withdrawal is regulated by a liquid-level controller installed in the reservoir section of the reboiler. This controller actuates a valve located in the discharge line immediately after the bottom product pumps, which are driven at constant speed by explosion-proof electrical motors.

Each reboiler is connected with the rectifying column by a single vapor line in which has been inserted an expansion head. A self-sealing liquid return line has been provided also, and in this manner the higher-boiling materials are returned to the reboiler with the minimum of contact with the escaping vapors. The rectifying columns have been placed on one common floor immediately above the reboilers and are so arranged that the minimum of piping exists between the reboiler and column. The fractionating columns vary in height and diameter according to the rectifying demands. [The comparative height of the fractionating towers is approximately indicated in the formalized flow diagram, Fig. 19.] The shell of the column is constructed of welded steel plate, and all interior fittings are of the same material. The material to be fractionated is fed into the column usually about midway between the base and top.[215]

A uniform design has been applied to the various condensers, product coolers, and bottoms coolers in order to minimize maintenance charges and spare-part inventories. The condensers are either four- or six-pass floating-head types made up of 1-inch 13-gage seamless black tube. The condensate drops by gravity to the coolers immediately below: these are usually two-pass floating-head types of 1-inch 13-gage seamless tube. In both devices the cooling water flows within the tubes while the vapors or condensed liquids are contained between the tube and shell. The interval of trouble-free operation between tube cleanings has been satisfactorily increased by the installation of a continuous filter in the main water supply line.

Continuous decanters or water separators have been installed in those units where water is likely to contaminate the distillate. The design is of the conventional fixed-weir type. The overflow of the decanter, or the discharge of the product coolers when no decanter is used, passes directly to a surge tank, equipped, like the reboilers, with a liquid-level-control actuating a valve in the discharge line of the distillate pump. The stream from the pump is divided, each branch being fitted with rotameters and appropriate manually operated valves.
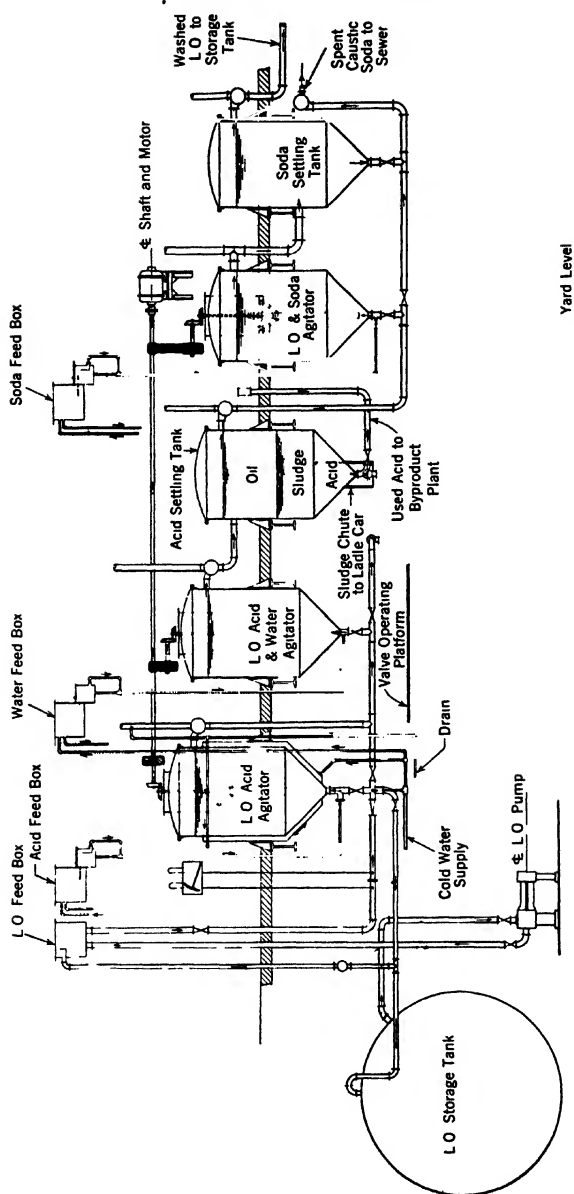
Fig 20 Flow diagram of a plant for the continuous acid washing of light oil.

The portion required for reflux is returned to the top plate of the rectifying column; the balance flows to storage tanks. It has been found desirable to equip some of the pure still units with a group of several small tanks; in this way an undesirable product due to inadvertent maladjustment of the apparatus may be diverted and the contamination of a large amount of satisfactory material already in storage avoided. The ultimate control of the units is based on suitable hourly analyses of all products.

The instrumentation and controls for each unit have been centralized as much as possible; almost all are incorporated in one panel on the operating floor. The instrumentation of some units is more elaborate than others, but, in general, a panel may include: an indicating and recording reboiler pressure gage, a reboiler steam controller, indicating steam and air-pressure gages, indicating level gages for depth of liquid in both the heating and reservoir sections of the reboiler, a constant feed rate controller, a six-point temperature indicating and recording instrument giving the temperature data of strategic parts of the system, and remote-control switches for the various transfer pumps. The overall steam and water consumption of the plant is continuously determined and recorded, and orifice plates for the individual units have been installed. Distillate and reflux flowmeters (rotameters) and the various valves necessary for regulation of reflux ratio and diversion of liquid streams to the appropriate parts of the system are located in the immediate neighborhood of the main control panel.

Although the plant described above, one of the few in America, was only put into operation in the '30's, it is interesting to note that the application of the continuous principle to light-oil fractionation was made

in the very early days of the industry.[216] Not many installations were made, and these, perhaps because of a lack of suitable automatic control equipment, were soon converted to intermittent operation. With few exceptions, over a long period, designers contented themselves with topical variants of the discontinuous system. However, there has been a trend, both at home and abroad,[161, 165, 217] towards continuous operations, and today no wholly discontinuous plants are built. The degree to which continuous fractionation is applied is a function of many variables, of which the most significant is the scale of the installation; for moderate sizes a compromise semi-continuous flow sheet seems most desirable.

The modern light-oil batch still maintains its place directly as a result of the improvements in fractionating effectiveness that have been made in the last decade. The batch stills of today show very little similarity to the best designs of the period 1910–30, which were essentially very large, horizontal cylindrical tanks surmounted by short stubby columns containing relatively few plates fitted with a small number of large bubble caps. The traditionally close spacing of the trays resulted in considerable entrainment with the correlative debasement of fractionating effectiveness. Reflux was obtained by means of dephlegmators, that is, partial condensers, mounted directly on the top of the column. The operation of dephlegmators was considered a fine art; it was believed by some that most of the separation occurred in the

[216] Goblet, A., *Die Fabrikation des Benzols aus Koksofengasen,* Verlag Fachliteratur, Berlin, 1914, 20 pp.

[217] Soc. des établissments Barbet, Brit. Pats. 244,130 (1924), 295,591 (1927), 380,348, 381,429 (1932); Ger. Pat. 567,834 (1925); Fr. Pat. 650,138 (1927).
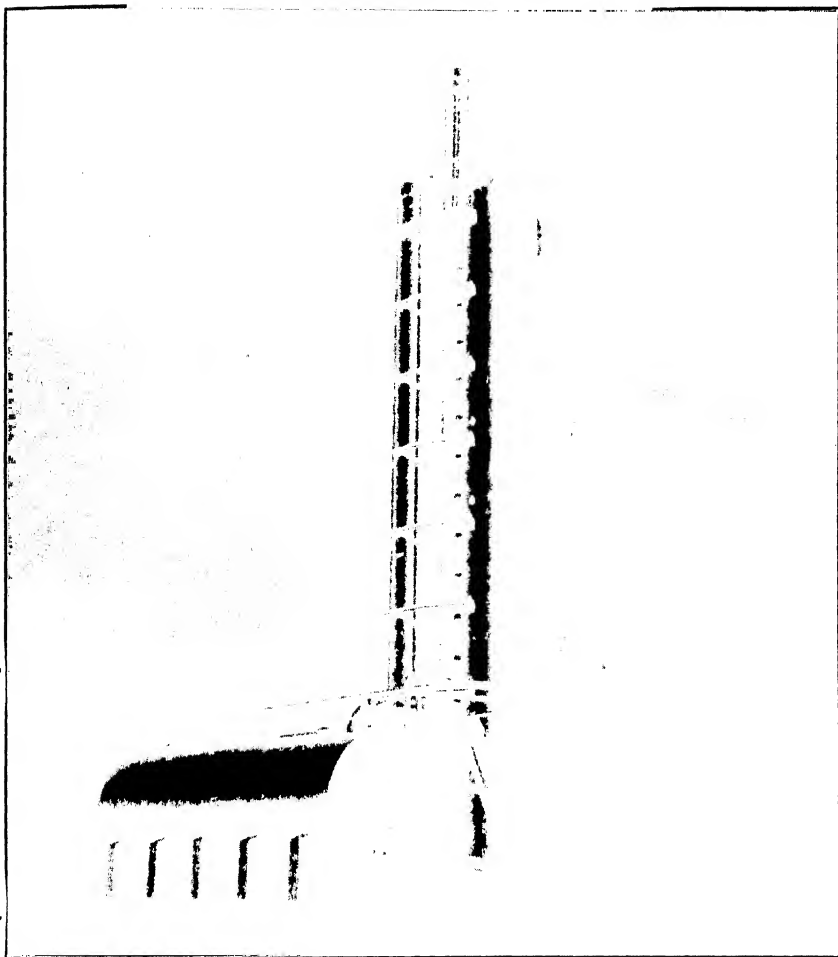
Fig 21. Medium-size semi-continuous light-oil refining plant.

partial condenser. In many cases, they may have been right. In the modern still, welded sheet steel has replaced cast iron as a material of construction; a multitude of caps per tray displaces the few previously used; a large number of well-spaced trays results in a slender, towering construction superseding the old stubbiness; total condensers, reflux pumps, and flow-meters make reflux ratio a controlled reality. Most important of all, the light-oil refiner has learned how to operate batch stills. Why they work the way they do remains an open question.

From the standpoint of technological architecture the new light-oil-refining plant is a great improvement over the old (Figs. 17 and 21). One does not regret, moreover, that light-oil plants have ventured into the open air and that the dark, traditional benzol house is rapidly disappearing. Protection from the weather can in most part be obtained by means of modern protective coatings, and buildings are held to a minimum, usually housing only acid washing equipment, pumps, and instrument and control panels. Design incorporating only a few enclosures is a definite contribution towards the safety of operating personnel.

Although quite a few antique •installations still survive, modernization is proceeding apace and the minutiae of these plants will soon be only of historical interest. The curious reader is referred to Gluud and Jacobson's *Handbook* [163] and similar works for details.

MISCELLANEOUS REFINING PROCEDURES

MOTOR BENZOL PROCESSES

Although no successful procedures, alternative to vigorous sulfuric acid treatment, have been developed for the manufacture of pure products, this statement is most certainly not true in respect to motor benzol refining. The attempts to solve the problem of the removal of gum formers with no accompanying loss of the innocuous unsaturates have produced an expenditure of much ingenuity and even more chemicals. Both commodities are well-nigh inexhaustible; the result is an enormous number of proposed processes, which may be roughly classified according to the principles of the methods employed: (1) sulfuric acid; (2) adsorbents; (3) polymerizing agents, such as halogens, hydrohalogen

acids, and chlorides; (4) oxidation; (5) hydrogenation; and (6) miscellaneous.[218]

SULFURIC ACID

Modifications of the sulfuric acid process assume many roughly equivalent forms such as the use of dilute acid or of very small quantities of strong acid. Of some interest, because of a limited application in American technology, are the Ufer process,[202] already described, and the Wagner-MacIntire process,[219] in which the light oil is washed with about 0.4 percent by volume of 66° Baumé sulfuric acid. After appropriate removal of sludge and neutralization the treated oil is distilled at a pressure sufficiently reduced to maintain the kettle temperature always below the decomposition point of gum-forming constituents and sulfur-containing hydrocarbons.

In Germany, the Stinnes [220] process has been widely employed. Eighty percent acid is used at temperatures below 40° C, and the washed material is distilled through hot caustic soda (essentially a vapor neutralizer). The general efficacy of 80 percent acid has been noted by several workers,[221] and reagent of approximately this strength defines several processes.[222] Ter-Nedden [223] noted that 80 percent acid-re-

[218] Much of the following is a condensation of Hoffert and Claxton's exhaustive treatment of this subject, ref. 6.

[219] Wagner, F. W., and MacIntire, F. L., U. S. Pat. 1,886,612 (1932).

[220] Gewerkeschaft Mathias Stinnes, Brit. Pat. 371,752 (1931); Ger. Pat. 672,959 (1939).

[221] Moehrle, E., *Brennstoff-Chem.*, **13**, 6–9 (1932). Weller, R., and Schramm, E., *ibid.*, **13**, 445–7 (1932).

[222] Oberschlesische Kokswerke u. chem. Fabr. A.-G., Ger. Pat. 421,558 (1922). Bayard, F. W., U. S. Pat. 1,474,136 (1923). Silica Gel Corp., Brit. Pat. 388,782 (1930). Concordia Bergbau A.-G., Brit. Pat. 380,495 (1931). Banta, C., Brit. Pat. 382,647 (1931).

[223] TerNedden, W., *Brennstoff-Chem.*, **19**, 101–3 (1938).

fined motor fuels were improved by the use of reduced pressure in the distillation step. Banta[224] and Jones[225] have patented processes in which only small quantities of concentrated or near concentrated acid are employed. The acid reagent itself may be modified by admixture with such materials as ferric sulfate,[226] phosphoric acid,[198] and alcohols or other solvents.[227] In the methods of the Société du gaz de Paris[228] the acid washing is carried out in the vapor phase, light-oil vapors being passed through porous masses impregnated with sulfuric acid. The process may be made continuous by flowing weak acid through a bed of refractory, countercurrent to the light-oil vapors. Dilute acid washing may be preceded by a wash with aqueous ammonia to improve color and odor.[229] It is to be noted that many of the processes utilizing other reagents usually involve a preliminary weak sulfuric acid wash for the removal of pyridine.

The bulk of the motor benzol fraction is relatively free of gum-forming constituents; the forerunnings and heavy ends, in which they are concentrated, may be removed for separate acid washing and later recombined with the untreated middle fraction.[230]

ADSORBENTS

The recovery of light oil by adsorption in a bed of silica gel has been described;[67] it is not surprising that proposals have been made for the application of this selective reagent to motor-benzol refining.[231] In an early form of the process, the light oil was given a light acid wash and then heated with very finely divided silica gel for periods of an hour or more. Spent adsorbent was removed by filtration and reactivated by heating to high temperatures. In a later development, the mild sulfuric acid treatment was followed by pressure filtration through a bed of silica gel maintained at 150° C. Neither technique seems to offer any advantage over a controlled weak acid washing procedure. Evers[232] has described a scheme consisting of treatment with ozonized air in the presence of silica gel, which adsorbs the resultant ozonides. The process is made continuous by causing the crude oil and reagent gas to flow countercurrently through a tower packed with the adsorbent. Parenthetically, it may be noted that ozone may combine with the aromatic hydrocarbons to form explosive materials.[233]

The Instill process,[234] which has seen some use in foreign practice, utilizes a compound reagent: a mixture of specially prepared active ferric sulfate, an adsorbent earth, and some free sulfuric acid. Pyridine poisons the purifying medium and is

224 Banta, C., U. S. Pat. 2,064,455 (1936).

225 Jones, I. H., U. S. Pat. 2,193,763 (1940).

226 Petroff, P. C., Fr. Pat. 726,516 (1931).

227 Hofmann, F., and Wulff, C., Brit. Pat. 301,420 (1928).

228 Soc. du gaz de Paris, Brit. Pats. 307,935, 314,052, 330,045 (1929).

229 Soc. anon. d'Ougrée-Marihaye, Brit. Pat. 435,965 (1934).

230 Pieters, H. A. J., and Visser, H. S., *Brennstoff-Chem.*, 12, 470-2 (1931).

231 Silica Gel Corp., Brit. Pats. 195,055 (1923), 292,231 (1927), 311,285 (1928), 373,174 (1931). Fulreader, R. E., *Ind. Eng. Chem.*, 21, 691-3 (1929). Geddes, R. C., *Gas World*, 94, Coking Sect., 9-12 (1931).

232 Siemens und Halske A.-G., Ger. Pat. 481,266 (1925).

233 Houzeau, A., and Renard, A., *Compt. rend.*, 76, 572 (1873). Renard, A., *ibid.*, 120, 1177-9 (1895). Harries, C., and Weiss, V., *Ber.*, 37, 3431-3 (1904).

234 Cox, K., and McDermott, P. J., Brit. Pats. 269,242 (1926), 303,991 (1927), 360,358 (1930); U. S. Pat. 1,658,285 (1928). Hatswell, F. T., *Gas World*, 88, Coking Sect., 11-4 (1928). Anon., *ibid.*, 94, 26-30 (1931), 97, 125 (1932), 102, 15-7, 41 (1935); *Iron Coal Trades Rev.*, 125, 570-1 (1932). Scott, T., Brit. Pat. 409,816 (1932). McDermott, P. J., Brit. Pat. 413,412 (1933).

first removed by a weak acid wash. The pyridine-free crude motor benzol is then preheated and pumped hot through a tower containing a mixture of medium and fine coke. The cooled material is washed with caustic and redistilled: a water white, gum-stable product results. Little or no reduction in thiophene content takes place; as a consequence, the process is inapplicable to high-thiophene crudes.

Mainz and Mühlendyck [235] have described a procedure utilizing fuller's earth or bleaching clay. Crude light oil is refluxed for 2 hours with 4 to 4.5 percent by weight of the adsorbent. A satisfactory motor fuel is distilled from the clay, in 95 percent yield. The oil and gums retained in the adsorbent are driven out by steam distillation; the oily distillate so obtained may be hydrogenated and also utilized as motor fuel. Variations in the effectiveness of the process with various stocks were noted: these were probably due to differences in the quantities of naturally occurring phenolic bodies (inhibitors) present in the finished products. Cox and McDermott previously had described a similar process.[236]

Refining by vapor-phase treatment with activated clays has long been familiar in the petroleum industry (the Gray process) and may also be extended to coke-oven light oil. One interesting variant comprises passing a mixture of light-oil vapors and steam through active clay; simultaneously and countercurrently, a high-boiling solvent is allowed to percolate through the bed. The solvent removes some of the adsorbed, gummy polymers and prolongs the activity of the adsorbent.[237] The vapor-phase clay

treatment may be preceded, as in many other of the motor-fuel processes, by a weak sulfuric acid wash.[238]

Active-carbon has been enumerated as an alternative in lists of refining adsorbents and carrier agents,[239] and its use in conjunction with oxidizing agents has been proposed.[240]

HALOGENS, HYDROHALOGEN ACIDS, AND METALLIC CHLORIDES

The reactive nature of these reagents makes them suitable not only in mild refining procedures but also in the preparation of pure products, and some of the processes described are directed to that end. In general the high cost and corrosive nature of these reagents have discouraged their commercial use.

Working with chlorine, Rabek [241] found that the reagent first attacked the unsaturates and then the sulfur compounds, the aromatics remaining unchanged. Freedom of the product from thiophene was claimed. A few processes utilizing chlorine have been proposed, most of which usually specify pretreatment with a limited sulfuric acid wash. The chlorinated residue resulting from the distillation of the treated oil may be used as a solvent.[242] Hofmann and Wulff used an alcoholic solution of hydrochloric acid; [227, 243] Universal Oil Products [244] em-

[235] Mainz, H., and Mühlendyck, W., *Brenn-stoff-Chem.*, **15**, 361–5 (1934).

[236] Cox, K., and McDermott, P. J., Brit. Pat. 246,210 (1924).

[237] Mandelbaum, M. R., U. S. Pat. 2,100,011 (1937).

[238] Lomax, E. J., and Lucas, O. D., Brit. Pat. 223,066 (1923); Ger. Pat. 460,472 (1928).

[239] Gutehoffnungshütte Oberhausen A.-G., Brit. Pat. 479,441 (1938).

[240] Richter und Richter, Ger. Pats. 240,760 (1910), 255,536 (1913). Prudhomme, E. A., U. S. Pat. 1,674,796 (1928).

[241] Rabek, T., *Brennstoff-Chem.*, **11**, 189–92 (1930).

[242] Seldon Co., Brit. Pat. 290,840 (1927); Fr. Pat. 636,485 (1928); U. S. Pat. 1,729,543 (1929). Riebeck'sche Montanwerke A.-G., Ger. Pat. 442,597 (1927).

[243] Hofmann, F., and Wulff, C., Brit. Pat. 298,484 (1928).

[244] Universal Oil Products Co., Brit. Pat. 395,-448 (1932).

ployed the latter reagent in the vapor form in the presence of brass, copper, zinc, iron, and other similar materials. Hofmann and Stegemann [245] treated the oil with 3 to 4 percent of hydrogen fluoride; metal halides such as boron fluoride might also be added. The reagent was readily recoverable, leaving a marketable pitch.[246]

Aluminum chloride, in addition to its strong polymerizing action, also induces condensations between the olefins and the aromatics, and various high-boiling materials, unsuitable as motor fuel, may be formed. The reagent can be used in the preparation of pure benzol, toluol, and xylol.[247] According to Kremer an equally good motor fuel can be obtained by treatment with 6 percent of 66° Baumé sulfuric acid or by refluxing with 2 percent of aluminum chloride for 5 hours. The aluminum chloride treatment is characterized by a much smaller process loss.[248] Ferric chloride,[249] zinc chloride,[250] stannous chloride,[251] and even the halides of beryllium, boron, and bismuth [252] have been proposed

as refining agents; needless to say, none have ever become economically interesting.

OXIDATION METHODS

Since gum formation in light oils and motor benzols is believed to take place through an initial oxidation step, one would expect that oxidizing agents could be employed in mild refining procedures.

Williams and Somerville [253] found that treatment with air or oxygen at 80° C and 200 pounds pressure, preferably in the presence of normal caustic soda, yielded a product that could be redistilled to give a satisfactory motor fuel. Dunkel [254] found that a 2-hour treatment with air at a temperature of 150° C and a pressure of 20 atmospheres was necessary and sufficient to bring about practically complete polymerization. The presence of either water or aqueous alkaline solutions was found to be immaterial. There was no reduction in thiophene concentration, and the product, dark brown in color, had to be redistilled. The same writer examined the phenomena attendant to passing crude light-oil vapors, mixed with air, over steel filings at 400 to 600° C. A high yield of motor fuel of good quality was obtained, although some oxidation of toluene and the higher homologs was observed. A practical application of these procedures was never made.[255] Downs [256] has devised a process which consists of passing a mixture of light oil in the vapor phase and an oxygen-containing gas (air) through a catalytic mass at a temperature between 250 and 550° C. Va-

245 Hofmann, F., and Stegemann, W., Brit. Pats 292,932–3 (1928).

246 Kattwinkel, R., Teer u. Bitumen, 26, 536 (1928).

247 Kopelevich, G. V., Brodovich, A. I., and Zhitomerskaya, E. N., Coke and Chem. (U.S. S.R.), 3, No. 7, 56–62 (1933); Chimie & industrie, 32, 315–6 (1935).

248 Kremer, M., Petroleum Z., 27, 459–61 (1931).

249 Demant, J., Ger. Pat. 392,090 (1917). Oberschlesische Kokswerke A.-G., Ger. Pat. 394,-217 (1923). Brückner, H., and Lang, A., Brennstoff-Chem., 16, 126–8 (1935). Carbo-Norit-Union Verw.-Ges., Brit. Pat. 447,533 (1935); Fr. Pat. 787,929 (1935).

250 Lachmann, A., U. S. Pats. 1,790,622, 1,-809,170 (1931); World Petroleum, 5, 384–6 (1934).

251 Mailhe, A., Compt. rend., 181, 668–9 (1925); J. usines gaz., 51, 104–6 (1927); Fr. Pats. 610,498–9, 611,890 (1925).

252 Hofmann, F., Dunkel, M., Otto, M., and Heyn, M., Ger. Pat. 550,429 (1926).

253 Williams, E. C., and Somerville, P. G., Brit. Pat. 219,351 (1923). The National Benzole Association, Rept. Joint Benzole Research Com., 1924, p. 114.

254 Dunkel, M., and Hofmann, F., Ger. Pat. 421,909 (1923). Dunkel, M., Brennstoff-Chem., 5, 145–9, 265–8 (1924).

255 Rosendahl, F., ibid., 20, 65–6 (1939).

256 Downs, C. R., U. S. Pat. 1,590,965 (1926).

nadium oxide is mentioned as a suitable catalyst.

Although the treatment of aromatics with ozone is not without hazard, Bruzac [257] found that a stable, colorless deodorized motor fuel could be obtained by comparatively mild exposure. About 100 volumes of ozonized air (8 to 10 grams of ozone per cubic meter) were blown, at atmospheric pressure and temperature, through each volume of benzene for a period not exceeding 1 hour. A brown precipitate was formed; this was removed and the treated material was washed with caustic and distilled. The process failed with some crude stocks; in all cases vapor losses to the treating air were large. Keller [258] removed hydrogen sulfide and hydrogen cyanide from light oils by aeration after a pretreatment with gaseous or aqueous ammonia. As a result, these impurities were converted to ammonium thiosulfate and ammonium thiocyanate, respectively.

Purification processes have been described based on the use of weakly acid potassium permanganate [259, 260] hydrogen peroxide,[261, 262] litharge, organic peracids,[262] and persulfates.[259] According to Herzenberg,[262] sulfur compounds are preferentially attacked by organic peracids and hydrogen peroxide, the unsaturates being relatively unaffected. In this connection it may be noted that, since the inhibitor process is not applicable to crude benzols containing more than 0.4 percent sulfur, as

thiophene, there is definite need for a simple and economic method of reducing the thiophene content of motor benzol without incurring a simultaneous loss of unsaturated hydrocarbons.

Little but novelty can be claimed for the electrolytic oxidation procedure of Gluud and Löpmann.[263] A mixture of 1 to 2 parts of crude and 1 part of 15 to 20 percent sulfuric acid was vigorously agitated in an electrolytic cell. The extent of purification was a function of current density, time of treatment, and the nature of the material. The presence of constituents boiling above 145° C seemed to have a beneficial effect on the degree of refining attained.[264]

HYDROGENATION

It is probably true that, through the choice of proper catalysts and operating temperatures, a hydrogenation technique can be employed with high-sulfur benzols to prepare satisfactory motor benzol in slightly higher yield than that of any other process. The increase in yield, however, would frequently be very small. (With low-sulfur crudes the inhibitor process provides a yield of 100 percent, and no other procedure can be economically competitive.) Hydrogenation is an expensive technique and has not been commercially employed for this purpose in America.

Carlile and Cawley [265] have reported on the application of hydrogenation to high-sulfur crudes. Desulfurization can be accomplished by hydrogenation at a pressure of 20 atmospheres and at a temperature of 350° C, with pelleted molybdenum sulfide

[257] Bruzac, J. F. A., Fr. Pat. 684,618 (1929).

[258] Keller, K., Ger. Pat. 566,036 (1930); *Ber. Ges. Kohlentech.*, **8**, 429–36 (1931).

[259] Moreau, J. L., Fr. Pat. 748,267 (1933).

[260] Guillet, O., Fr. Pat. 761,454 (1934). Kárpáti, G., and Schay, G., Austrian Pat. 142,584 (1935).

[261] Kwal, B., *Chimie & industrie*, **35**, 1040–4 (1936).

[262] Herzenberg, J., Brit. Pats. 424,616, 424,564 (1933); Fr. Pat. 758,567 (1934); *Erdöl u. Teer*, **9**, 436–9, 448–51, 460–3 (1933).

[263] Gluud, W., and Löpmann, B., Ger. Pat. 566,037 (1930). Gluud, W., Löpmann, B., and Keller, K., *Ber. Ges. Kohlentech.*, **4**, 82–95 (1931).

[264] Schuster, F., *Gas- u. Wasserfach*, **75**, 649 (1932).

[265] Carlile, J. H., and Cawley, C. M., *J. Soc. Chem. Ind.*, **57**, 347–9 (1938).

as a catalyst. The refining losses are about 3 percent; the octane number is reduced from 105 to 103.

Very many patents have been issued for the purification of hydrocarbons by vapor-phase hydrogenation; some of these are particularly applicable to aromatics, either for pure product preparation or for mild refining procedures.[266] Among the catalysts mentioned are oxides and sulfides of the sixth group and various tin, vanadium, rhenium, manganese, zinc, cadmium, aluminum, and cobalt compounds. Catalysts of the nickel type are rapidly poisoned by small amounts of thiophene.[267]

Rostin's hydrogenation process is novel in that an impurity furnishes the reagent.[246] A copper-aluminum couple reacts with the hydrogen sulfide present in the material; the resultant nascent hydrogen in turn reacts with the gum-forming unsaturates. In another variation [268] the nascent hydrogen is prepared by passing hydrogen sulfide over silver precipitated on asbestos or pumice. In a later modification, hydrogenation is effected by passing the hydrocarbon vapors with hydrogen sulfide over freshly reduced iron at 200° to 300° C.[269] In a still more recent invention, hydrogen sulfide is first removed and hydrogenation may be dispensed with; today the "Rostin process" usually refers to vapor-phase

treatment at 350° C with a finely divided iron ore (minette).[270]

In the procedure of Henderson the crude stock is refluxed with sulfuric acid and zinc dust or with strong alkali and zinc. The oil is separated, treated with strong sulfuric acid, and finally distilled.[271] It is claimed that purification is brought about by the presence of nascent hydrogen formed through the reaction with the metal. Nascent hydrogen is also utilized by d'Hercourt,[272] who brings the crude into contact with an aluminum-mercury couple.

MISCELLANEOUS PROCEDURES

Mansfield [172] in 1849 was able to obtain quite pure benzol by freezing his crude material and pressing the crystals relatively free of mother liquor. It has been pointed out [214] that a crystallization procedure has been successfully applied in this country in the manufacture of highly pure, reagent-grade benzol. Naphtali has described the application of this principle to the preparation of motor benzol.[273] Yields are of the order of magnitude of 80 percent, the 20. percent noncrystallizable mother liquor being further refined by distillation and destructive hydrogenation. Separation of crystals and liquid is accomplished by centrifuging. Vita [274] had previously described an essentially similar process.

It has been claimed that satisfactory purification can be obtained by simply heating crude light oil under pressure, to temperatures in the range 100 to 320° C.[255, 275] The gum-forming diolefins

266 I. G. Farbenindustrie A.-G., Brit. Pats. 257,576 (1925), 258,576 (1926), 315,439, 327,194 (1928), 418,941 (1933). Otto, C., and Co., G.m. b.H., Fr. Pat. 677,806 (1928). Howes, D. A., Norris, W. S. G. P., and Henderson, S. T., Brit. Pat. 343,359 (1930). Ges. Teerverwertung m.b. H., Ger. Pat. 641,172 (1937). Gwynn, M. H., U. S. Pat. 2,106,735 (1938).

267 Kubota, B., and Yoshikawa, K., *Sci. Papers Inst. Phys. Chem. Res.* (*Tokyo*), **3**, 35-50 (1925); *Japan. J. Chem.*, **2**, 45-62 (1925). Roberti, G., *Gazz. chim. ital.*, **63**, 46-9 (1933).

268 Rostin, H., Fr. Pat. 613,101 (1925).

269 Rostin, H., Brit. Pat. 286,255 (1927). Thau, A., *Glückauf*, **71**, 298-304 (1935).

270 Thau, A., *Coal Carbonization*, **5**, 37-40 (1939).

271 Henderson, S. T., Brit. Pat. 350,494 (1930).

272 d'Hercourt, M., Fr. Pat. 736,378 (1931).

273 Schuftan, P., Ger. Pats. 622,727, 628,837 (1935). Naphtali, H., *Refiner Natural Gasoline Mfr.*, **16**, 224-6 (1937).

274 Vita, A., Ger. Pat. 384,846 (1919).

275 Schlesisches Kohlenforschungsinstitut der Kaiser-Wilhelm-Ges., Brit. Pat. 226,188 (1923). Schmidt, H., Ger. Pat. 602,034 (1934).

are polymerized while the aromatics and monoölefins remain unchanged. A light sulfuric acid wash (to remove pyridine) precedes the heat treatment, which is carried out in suitable autoclaves. This process differs from most of the others described in this section in that it is simple and economically feasible. Rühl recommended a modification involving the use of catalytic bodies during the heat-pressure polymerization.[276]

Ultraviolet light[277] and electric discharges[278] might be expected to have some effect, and their use has been patented for hydrocarbon refining.

According to Uloth,[279] a satisfactory motor fuel, stable to light and free of gumformers, may be obtained by adding 1.5 percent of sulfur and heating for 2 hours at 230° C in an autoclave. In addition to sulfur,[280] heavy metal sulfides such as iron sulfide[281] and copper sulfide[282] have been proposed as refining agents.

Many processes are based on the use of acidic substances. A partial list would include: oleic acid followed by sulfuric acid,[283] phenols and cresols,[284] maleic acid and maleic anhydride,[285] paraffin monocarboxylic acids,[286] boric acid,[287] pyrosulfates,[288] nitric acid followed by sulfuric acid,[289] and chlorosulfonic acids.[290] Aldehydes,[291] aldehyde polymerides, or substances which produce aldehydes in the presence of polymerizing agents may be used as refining reagents, the impurities containing sulfur being precipitated in an insoluble form. Diametrically opposed in expense as reagents are alkaline dust obtained from blast-furnace slag[292] and the alkali metals.[293] It may be noted here that inhibitors are frequently used in mild refining procedures, the addition of the inhibitor being the final step of the process.

Supplementary and Alternative Refining Methods

In both pure products and motor-fuel refining it is sometimes desirable to introduce a purification step directed more or less emphatically at one particularly obnoxious compound. Such processes, usually isolated parts of a more general and comprehensive refining scheme, can be conveniently grouped and enumerated in definite classes according to the specific impurity involved. Thus we have methods for the

[276] Rühl, G., *Brennstoff-Chem.*, **18**, 413–20 (1937), **19**, 1–12 (1938).

[277] Goltstein, G., Brit. Pat. 249,895 (1924). Davis, R. F., U. S. Pat. 1,551,806 (1925). McConnell, J. R., U. S. Pat. 1,590,841 (1925). Bruzac, J. F. A., Fr. Pat. 766,060 (1934).

[278] Thomas, D. L., U. S. Pat. 1,585,573 (1926). Chem. Fabrik Libenia G.m.b.H., Ger. Pat. 495,-271 (1927). I. G. Farbenindustrie A.-G., Brit. Pat. 409,813 (1932).

[279] Uloth, R., *Brennstoff-Chem.*, **10**, 297–301 (1929).

[280] Egloff, G., U. S. Pat. 1,896,227 (1933). Higgins, E. C., Jr., and Gardner, F. J., U. S. Pat. 1,977,631 (1934).

[281] Pschorr, R., Ger. Pat. 380,059 (1923).

[282] Kiemstedt, H., Ger. Pat. 640,204 (1936).

[283] Petroff, G., Brit. Pat. 291,823 (1927).

[284] Gutehoffnungshütte Oberhausen A.-G., Fr. Pat. 829,221 (1938).

[285] I. G. Farbenindustrie A.-G., Brit. Pat. 352,-164 (1930).

[286] Deutsche Erdöl A.-G., Ger. Pat. 352,917 (1922).

[287] Jaeger, A., *Brennstoff-Chem.*, **4**, 260–1 (1923). Kattwinkel, R., *ibid.*, **8**, 353–8 (1927). Cornic, Y., Fr. Pat. 724,324 (1932).

[288] Plauson's Forschungsinstitut G.m.b.H., Ger. Pat. 352,189 (1922).

[289] Hense, R., Fr. Pat. 618,302 (1927). Société H/H Oil Co., Akts., Ger. Pat. 691,430 (1930).

[290] Shepard, A. F., and Henne, A. L., *Ind. Eng. Chem.*, **22**, 356–7 (1930). Oranienburger chem. Fabr. A.-G., Ger. Pats. 594,555, 600,251, 605,802 (1934).

[291] Ormandy, W. R., and Craven, E. C., *J. Inst. Petroleum Tech.*, **10**, 99–100 (1924). A. Riebeck'sche Montanwerke A.-G., Ger. Pat. 439,-608 (1927). Morgan, G. T., and Pettet, A. E. J., Brit. Pat. 397,847 (1933).

[292] Rochling'sche Eisen- und Stahlwerke G.m.b.H., Ger. Pat. 654,826 (1937).

[293] Hütz, H., Ger. Pats. 374,928 (1920), 385,-761 (1922).

elimination of carbon disulfide, thiophene, mercaptans, etc.

CARBON DISULFIDE

The removal of carbon disulfide is frequently mandatory in the successful application of the inhibitor motor-fuel process; in American practice the separation is universally accomplished by efficient fractional distillation. In British practice, before the use of forerunnings strippers became common, emphasis was placed on chemical procedures and two interesting methods were employed on a large scale: the "methanol-soda" [294] and the "ammonium polysulfide" processes.

In the former, use is made of the reaction:

$$NaOH + CH_3OH + CS_2 \rightarrow NaSCSOCH_3 + H_2O$$
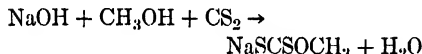
which is a practical adaptation of the ethyl alcohol-potassium hydroxide reagent long used by analysts for the estimation of carbon disulfide. Methyl alcohol, unlike ethyl alcohol, forms no azeotrope with water, and its recovery in high concentration by fractional distillation materially contributes to the practical utility of the process. The treatment with the reagent is usually carried out in a standard acid-washing agitator, most conveniently immediately after any washing step. The requisite amount of 95 percent methanol, the exact quantity being a function of the carbon disulfide concentration, is added to the benzol; this is followed by the slow addition of solid flake caustic soda, agitation being continued throughout. After 2 or 3 hours of agitation and reaction, the xanthate is extracted by washing the mixture two or three times with water. The washed benzol is then redistilled. The aqueous residues are neutralized with sulfuric acid under carefully controlled conditions and fractionally batch-distilled. Both the neutralization and distillation steps are accompanied by the evolution of noxious gases, mostly hydrogen sulfide, and in increased quantity if the residues have been stored for any length of time. The overall effect of the regeneration step is to recover about 85 percent of the methanol originally employed in a form suitable for reuse; in addition about 60 percent of the carbon disulfide removed is recovered as a nearly colorless distillate containing approximately 90 percent of carbon disulfide.

In the ammonium polysulfide process [295] the removal of carbon disulfide is accomplished by agitating the benzol in a standard washer with a reagent consisting of approximately equimolecular proportions of ammonium disulfide, ammonium sulfide, and free ammonia. The benzol is usually washed first with a once-used reagent, which is then suitably separated and the operation repeated with a portion of fresh reagent. A final wash with water completes the process, no redistillation of the treated oil being necessary. The spent reagent is regenerated by simple distillation. Some of the reactions that take place may be:

Absorption:

$$(NH_4)_2S_2 + CS_2 = (NH_4)_2CS_4$$
$$(NH_4)_2S + CS_2 = (NH_4)_2CS_3$$

Regeneration:

$$(NH_4)_2CS_4 \rightarrow 2NH_2 + CS_2 + H_2S + S$$
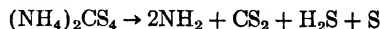
The reagent is prepared by passing hydrogen sulfide in suitable quantity into a

294 Hoffert, W. H., and Hancock, E. G., Brit. Pats. 416,404, 428,931 (1933). Wikner, S. W. A., and Richardson, B., Gas J., 206, 559–67 (1934). Hoffert, W. H., Claxton, G., and Hancock, E. G., J. Soc. Chem. Ind., 54, 239–46T (1935). Adam and Anderson, ref. 8.

295 Yorkshire Tar Distillers Ltd., Brit. Pat. 419,312 (1933).

suspension of sulfur in aqueous ammonia. During regeneration, after removal of the carbon disulfide (which appears first), the liberated ammonia and hydrogen sulfide are absorbed in water as a solution of ammonium sulfide, the sulfur remaining in the still. The sulfur residue is redissolved by circulating the ammonium sulfide solution through the heated kettle. When solution of the sulfur is complete, ammonia is added and the reagent is again ready for use, the addition of fresh hydrogen sulfide being usually unnecessary. Part of the successful application of this process was due to the marketing policy of the owners; both the preparation of fresh reagent and the regeneration of spent material were carried out at a central plant.

Actual commercial utilization of chemical processes seems to be restricted to the two described above. A variety of others have been proposed, namely: agitation at 65 to 68° C with a 10 percent solution of caustic soda,[296] treatment with alkali cellulose,[297] treatment with aqueous ammonia,[229, 298] and aqueous solutions of ammonia and caustic soda,[299] extraction with cold solutions of alkaline-earth disulfides,[300] and heating in an autoclave with aqueous caustic soda or an alkaline earth.[301] Somewhat more promising are the recent applications of organic reagents such as piperidene,[302] piperidene pentamethylenedithio-

carbonate in the presence of magnesium oxide,[303] and morpholine.[304]

THIOPHENE

If the forerunnings, and thereby all the carbon disulfide and hydrogen sulfide, are carefully removed from coke-oven light oil and the total sulfur content of the following benzol, toluol, and xylol fractions determined, it is found that the distribution of sulfur compounds is substantially uniform throughout the light oil. Almost all the sulfur in the benzol fraction exists as thiophene; there is some evidence to indicate that the sulfur compounds in the toluol and xylol fractions are the corresponding homologs of this compound. Disulfides, sulfides, and mercaptans are quite unstable at the temperatures of coke-oven atmospheres and readily decompose to hydrogen sulfide, thiophene, and thiophene derivatives. Accordingly, the disulfide, sulfide, and mercaptan content of crude high-temperature coke-oven light oils is vanishingly small. Thiophene, by contrast, is completely stable at 870° C [13] and perhaps higher. •

Thiophene removal is often important in the production of motor fuel and, by definition, mandatory in the preparation of thiophene-free pure benzol. The two problems are, however, essentially different.

The motor-fuel manufacturer, working with high-sulfur crudes, is interested only in a reduction of thiophene content sufficient to meet sulfur specifications. Further, this is to be accomplished with the minimum concomitant destruction of unsaturates. The pure benzol refiner, on the other hand, finds it necessary to reduce the thiophene concentration to 0.0005 percent

296 Wilson, J. A., *Gas World*, **69**, No. 1794, Coking Sect., 13–5 (1918); *Gas J.*, **144**, 465–7 (1918); Brit. Pat. 14,152 (1915).

297 Kipper, H. B., U. S. Pat. 1,253,048 (1917).

298 Thompson, J. E., U. S. Pat. 1,276,284 (1918).

299 Sontag, B. D., U. S. Pat. 2,165,732 (1939).

300 Forwood, G. F., and Taplay, J. G., Brit. Pat. 129,349 (1917). Colman, H. G., and Yeoman, E. W., Brit. Pat. 145,099 (1918). Klaiber, W. J., U. S. Pat. 1,785,415 (1930).

301 Gewerkschaft Mathias Stinnes, Brit. Pat. 425,938 (1934).

302 Belford, J. S., Brit. Pat. 453,340 (1936).

303 Parkes, D. W., and Mitchell, C. D., Brit. Pat. 467,581 (1935); *J. Soc. Chem. Ind.*, **57**, 113–6 (1938).

304 Schulze, W. A., U. S. Pat. 2,045,057 (1936).

("thiophene-free") or less. Present-day nitration benzols, refined in the ordinary manner, without special treatment, may contain from 0.005 to 0.015 percent of thiophene. This seemingly small quantity rapidly poisons the nickel-type catalysts used in such processes as the hydrogenation of benzene to cyclohexane and introduces complications in the manufacture of dye intermediates. Since unsaturates must, by specification, be completely removed from pure benzols, it is necessary only that the reagent used should not significantly attack aromatics and that the process be otherwise economically feasible.

Physical means of thiophene removal have met with little success. Although thiophene forms no azeotrope with benzene,[305] the small difference in the boiling points of benzene and thiophene and the low initial concentration of thiophene would lead one to expect that purification by fractional distillation would require very effective equipment; in practice this prediction is realized, and it is found that no significant separation can be obtained in conventional apparatus. Crystallization is unfortunately not readily applicable. Although isomorphism does not exist between benzene and thiophene, there is a strong similarity in form and in the dimensions of the elementary cell; accordingly, the phase diagram exhibits a continuous series of solid solutions [306] (isodimorphism).

Although many chemical processes have been proposed, sulfuric acid washing [307] so far represents the most feasible procedure and is the only method widely employed. In motor-benzol refining, since the unsaturates are also destroyed, it is desirable to use only enough acid to effect the desired reduction in thiophene content. Within limits, the same yield of motor fuel will be obtained for a given removal of thiophene, irrespective of the quantity and strength of acid used to effect this removal.[26] The mechanism of thiophene removal seems to depend upon the condensation of thiophene with unsaturates,[24] and the extent of purification obtained with any given treatment will depend upon the nature and quantity of the unsaturates present. The amylenes are particularly effective. Some workers have suggested the addition of cyclopentadiene to the light oil or benzene before washing.[308] In removing the trace quantities involved in refining nitration benzol to "thiophene-free" grades, it is found that only the most concentrated acids are effective. Fuming sulfuric acid is frequently used.

The use of anhydrous aluminum chloride was suggested as early as 1894.[309] None of the processes [310] subsequently developed have found commercial utilization. In the reaction between thiophene and aluminum chloride, a reddish viscous sludge is formed which tends to adhere to the surface of the aluminum chloride. Anhydrous conditions are necessary as very small quantities of water seriously reduce the effectiveness of

305 Świętowsławski, W., and Usakiewicz, J., Roczniki Chem., 13, 495–9 (1933).

306 Paterno, E., Gazz. chim. ital., 19, 640, 666 (1889). Bechmann, E., Z. physik. Chem., 22, 609–18 (1897). Tsakalotos, D. E., and Guye, P. A., J. chim. phys., 8, 340–57 (1910). Bruni, G. and Natta, G., Rec. trav. chim., 48, 860–3 (1929).

307 Meyer, V., Ber., 15, 2893–4 (1882), 16, 1465–78 (1883). Ellerton, J. G., J. Soc. Chem. Ind., 31, 10–2 (1912). Wood, A. E., Lowy, A.,

and Faragher, W. F., Ind. Eng. Chem., 16, 1116–20 (1924). Wood, A. E., Sheely, C., and Trusty, A. W., ibid., 18, 169–71 (1926).

308 Kopelevich, G. V., and Brodovich, A. I., Russ. Pat. 39,096 (1934).

309 Soc. anon. des matières colorantes de St. Denis, Fr. Pat. 240,111 (1894); Ger. Pat. 79,505 (1894).

310 Haller, A., and Michel, E., Bull. soc. chem., 15, 390, 1065–70 (1896). Heusler, F., Z. angew. Chem., 9, 288, 318, 750 (1896); Brit Pat. 4,769 (1897).

the reagent. Holmes and Beeman [311] recommended successive treatments at the moderate temperatures of 25 to 35° C, in the belief that the aluminum chloride acts in the dual capacity of chemical reagent and physical absorbent, the latter function being considered to be impaired at higher temperatures. A redistillation of the benzol should be carried out between successive treatments with aluminum chloride. Chlorination by use of gaseous chlorine or an aqueous solution has also been proposed.[312] Large benzene losses are experienced.

The mercuration of thiophene is relatively easy, and many attempts have been made to exploit this reaction, as the basis of a suitable analytical method.[313] Unfortunately, this procedure fails to give reliable results in the presence of unsaturates, a disadvantage shared with methods based on the familiar isatin reaction.[314] Ardagh and Furber found that benzene could be effectively freed of thiophene by refluxing with a mixture of mercuric oxide and stearic acid.[315] The costly reagent limits this process to the laboratory. The substitution of zinc oxide, magnesium oxide, and lead oxide gave negative results.

The invention of Ardagh and Bowman [316]

seems to possess the requirements of a successful commercial process. Complete removal of thiophene is obtained by agitation for 15 minutes at room temperature with a mixture of calcium hypochlorite and acetic acid in the mole ratios of thiophene, 1; hypochlorite ion, 5; acetic acid, 16. The benzene layer (colored greenish yellow) is washed with alkali and fractionally distilled. The active agent is hypochlorous acid; sodium hypochlorite alone is without effect.[317]

The removal of thiophene can be effected by hydrogenation using such catalysts as nickel and cobalt oxides,[318] molybdenum trioxide, zinc oxide,[319] and an equimolecular mixture of cobalt sulfide and molybdenum oxide.[320] Rapid poisoning of the catalyst occurs. Hydrogenation (with nickel catalysts) is relatively more efficacious in the removal of mercaptans and sulfides.[321] Favorable claims have been made for the following: treatment with bromine;[322] condensation with formaldehyde, acetaldehyde, and phthalic anhydride;[323] treatment with alkaline permanganate;[324] heating to 1,000° F in the presence of an inert gas;[325] treatment with iron hydroxide;[326] autoclaving;[327] vapor-phase oxidation,[256]

[311] Holmes, H. N., and Beeman, N., *Ind. Eng Chem.*, **26**, 172–4 (1934).

[312] Willgerodt, C., *J. prakt. Chem.*, (3), **33**, 479 (1886). Dutt, P. K., and Hamer, J. D., Brit. Pat. 117,683 (1917). Hamer, J. D., *Gas World*, **68**, No. 1763, Coking Sect., 13–6 (1918).

[313] Denigès, G., *Bull. soc. chim.*, **13**, 537–46 (1895), **15**, 862–71, 1064–5 (1896). Dimroth, O., *Ber.*, **32**, 758–65 (1899), **35**, 2032–45 (1902). Paolini, V., *Gazz. chim. ital.*, **37**, I, 58 (1907). Paolini, O., and Silberman, B., *Ann. chim. applicata.*, **4**, 289 (1915). Spielmann, P. E., and Schotz, S. P., *J. Soc. Chem. Ind.*, **38**, 188-90T (1919).

[314] Schwalbe, C., *Chem.-Ztg.*, **29**, 895–6 (1905). Meyer, A., *Compt. rend.*, **169**, 1402–4 (1919).

[315] Ardagh, E. G. R., and Furber, C. M., *J. Soc. Chem. Ind.*, **48**, 73-5T (1929).

[316] Ardagh, E. G. R., and Bowman, W. H., *ibid.*, **54**, 267-8T (1935). Ardagh, E. G. R.,

Bowman, W. H., and Weatherburn, A. S., *ibid.*, **59**, 27 8 (1940).

[317] Wood, A. E., Green, A. R., and Provine, R. W., *Ind. Eng. Chem.*, **18**, 823–6 (1926).

[318] Orlov, N. A., and Broun, A. S., *Khim. Tverdogo Topliva*, **3**, 817–24 (1932).

[319] I. G. Farbenindustrie A.-G., ref. 266.

[320] Pease, R. N., and Keighton, W. B., *Ind. Eng. Chem.*, **25**, 1012–3 (1933).

[321] Elgin, J. C., *ibid.*, **22**, 1290–3 (1930).

[322] Meyer, V., and Stadler, O., *Ber.*, **18**, 1488–90 (1885).

[323] Badische Anilin Soda Fabrik, Ger. Pat. 211,239 (1909).

[324] Donath, E., and Ditz, H., *J. prakt. Chem.*, **60**, 574–6 (1899).

[325] Evans, O. B., Brit. Pat. 112,878 (1917).

[326] Reeson, J. N., and Moss, W. L., Brit. Pat. 249,312 (1925).

[327] Dunkel, ref. 254.

treatment with anhydrous hydrogen iodide,[328] and reduction with carbon monoxide.[329] Effective thiophene removal is also claimed in many of the motor-fuel-refining processes previously described.

ANALYTICAL METHODS

Recent compilations of analytical procedures useful in the light-oil industry are those of Glowacki and of Altieri, both of which give in detail the various procedures that have been developed.[330]

[328] Nellensteyn, F. J., *Chem. Weckblad*, 24, 102–5 (1927).

[329] Cawley, C. M., *J. Inst. Petroleum Tech.*, 23, 209–12 (1937).

[330] Glowacki, W. L., *The Determination and Examination of Light Oil· in Gas*, Am. Gas Assoc., New York, 1941, 40 pp.; *Proc. Am. Gas Assoc.*, 1941, 449–50. Altieri, V. J., *Gas Chemists' Book of Standards for Light Oil and Light Oil Products*, Am. Gas. Assoc., New York, 1943, 352 pp.

REMOVAL OF MISCELLANEOUS CONSTITUENTS FROM COAL GAS

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In other chapters of this book the subject of removal of various constituents from coal gas has been discussed in some detail. The constituents so discussed include nitrogen compounds, such as ammonia and hydrocyanic acid (Chapter 27), sulfur compounds, such as hydrogen sulfide and organic sulfur (Chapter 26), and the mixture of hydrocarbon and other vapors known as "light oil" (Chapter 28). Of less relative importance are processes for the removal from coal gas of various other constituents, and the application of extraction processes to them in coal gas is not universal by any means. Removal of naphthalene is fairly common, but planned and systematic removal of the other constituents is rare. In the present chapter, processes for removal of the following constituents are discussed: (1) naphthalene; (2) indene, styrene, etc.; (3) ethylene; (4) hydrogen; (5) carbon monoxide; (6) nitric oxide; and (7) water vapor.

As in all other extractions of compounds from gas, the incentive for carrying on the process may be included in one of three classes: (1) the removed constituent is objectionable if left in the gas; (2) the removed constituent is a useful byproduct; or (3) a combination of 1 and 2. The matter of the incentive will be discussed under each subject.

REMOVAL OF NAPHTHALENE

Naphthalene is formed in relatively large quantities during high-temperature carbonization of coal, but in much smaller quantity or not at all at low carbonization temperatures. However, since coal gas is produced commercially almost universally at high carbonization temperatures, naphthalene is one of the chief compounds coming over with the volatile products from the carbonization chamber.

The boiling point of naphthalene is quite high (218° C), and its vapor pressure is relatively low at the temperature of the condensation system of a coal-gas plant, so that it is almost entirely condensed with the tar. The large amount of naphthalene coming from the high-temperature carbonization of coal can be well illustrated by the fact that tar contains in the order of 10 percent of naphthalene, by far the largest percentage of any single chemical compound present in coal tar.[1]

Because of this relatively high percentage of naphthalene in coal tar, the amount of naphthalene remaining in the gas as vapor is not very far removed from the saturation point, and, as the gas is further cooled, the saturation point is finally reached. This is illustrated by the fact

[1] Weiss, J. M., and Downs, C. R., *Ind. Eng. Chem.*, **15**, 1022–3 (1923).

that there is usually a scum of naphthalene crystals on the surface of the cooling water coming from a direct final cooler.

However, the most serious effect of naphthalene in coal gas is its tendency to deposit as crystals of solid naphthalene in the gas-distribution system as the gas is carried to lower temperatures after leaving the plant. Such solid deposits may gradually grow in size until gas pipes of the distribution system are filled at certain points and stoppage of gas flow may result. Because of this phenomenon the vapor pressure of naphthalene at different temperatures is of more than ordinary importance, and various determinations have been made by different investigators, using coal gas as the carrying medium.

The quantity of naphthalene required to saturate coal gas at definite temperatures has been determined by both Allen[2] and Schlumberger,[3] and was later carefully checked by Thomas.[4] The determinations of Thomas are in substantial agreement with data used today. Thomas found that the quantity of naphthalene required to saturate dry coal gas at a pressure of 760 millimeters depended on the temperature as shown in Table I. The equivalent vapor pressures of naphthalene are in reasonably close agreement with vapor-pressure data for naphthalene as determined by other and more accurate methods used more recently.

The completeness of removal of naphthalene from coal gas before the gas can be distributed with no fear of solid deposits coming out in the distribution system is determined by the minimum temperature to which the gas will be subjected during

2 Allen, R. W., *J. Soc. Chem. Ind.*, **19**, 209–13 (1900).

3 Schlumberger, E., *J. Gasbeleucht.*, **55**, 1257–60 (1912).

4 Thomas, J. S. G., *J. Soc. Chem. Ind.*, **35**, 506–13 (1916).

TABLE I

NAPHTHALENE SATURATION OF COAL GAS [4]

Temperature °C	Naphthalene grains per 100 cubic feet of gas	Equivalent Vapor Pressure millimeters of mercury
0	1.85	0.0056
5	3.26	0.0101
10	5.59	0.0175
15	9.39	0.0300
20	15.5	0.0505
25	25.2	0.0835
30	40.3	0.136
40	98.5	0.344
50	227	0.815
60	497	1.84

its travel in the mains and service pipes. For example, if it is known that the gas will never reach a temperature as low as 10° C, then removal of the naphthalene down to 5 grains per 100 cubic feet would be sufficient, since this quantity would correspond to a naphthalene dew point below 10° C. Usually an attempt is made to lower the naphthalene content to 3 grains or less per 100 cubic feet, and under cold-weather conditions the amount left in the gas before distribution may be as low as 1 grain per 100 cubic feet to insure absence of stoppages due to deposited naphthalene.

Since the amount of naphthalene present in coal gas after ordinary condensation methods have been applied to the gas is of the order of 15 to 50 grains per 100 cubic feet, the efficiency of removal in order to make the coal gas safe for distribution must be about 90 percent or higher. It should be emphasized that the purpose of removal is entirely to prevent distribution trouble and not for recovery of naphthalene as a byproduct.

In various textbooks and special articles there have been presented the general principles and descriptions of processes for re-

moval of naphthalene from gas.[5, 6, 7, 8, 9, 10, 11] Methods for naphthalene removal may be classified into four general groups: (1) condensation by cooling; (2) absorption by solvents in a washer or scrubber; (3) application of solvents, either in liquid or vapor form, to the gas-distribution mains; and (4) adsorption by solids.

The first three, at least, of these processes apply to a limited extent in normal manufacture of coal gas or other manufactured gas, even though removal of naphthalene is not specifically sought. Thus, coal gas is always cooled after leaving the ovens or retorts, and considerable condensation of naphthalene occurs during this operation. Coincident with the cooling, the condensation of tar is accompanied by some absorption of naphthalene by the tar. Also, later in the gas-distribution system, certain oils condense from the gas and carry naphthalene in solution as they run to the drip collecting points. If it were not for these "natural" or coincidental processes that remove a portion of the naphthalene from the gas, deposition of naphthalene in the gas-distribution system would be a major problem and it would be neces-sary to install removal equipment in all coal-gas plants. As it is, however, many gas operations are able to control naphthalene within fairly reasonable limits by proper attention to the normal cooling operations; others must, of necessity, install special equipment for satisfactory removal of the naphthalene.

Condensation by Cooling. If coal gas is cooled in the plant to a temperature that is equal to or less than the lowest temperature to which it will be subjected in the distribution system there will be no deposition of naphthalene in the gas lines. In most gas plants this is not possible without providing artificial refrigeration. In rare cases, large volumes of cold cooling water are readily available, and efficient removal of naphthalene may be secured without trouble. However, it is quite generally recognized today that the conditions of condensation have much to do with efficient removal of naphthalene and that, with the same amount of cooling water at equal temperatures, quite different removal efficiencies may be attained, depending on how the cooling is carried on.

"Shock," or quick, condensation is favored over slow condensation when maximum naphthalene removal is desired. The relationship of this speed of cooling to naphthalene removal has been discussed by Haug,[12] who explained slow condensation as that taking place in two or more stages with the condensate removed after each stage, whereas "shock" condensation takes place in one stage with the condensed liquids carried along in the gas stream until condensation is complete. This fine mist contains condensed tar, and the intimate contact between the tar mist and the gas permits the tar to act as a fairly efficient naphthalene solvent. The greater efficiency

5 Meade, Alwyne, *Modern Gas Works Practice,* Benn Bros., London, 1921, pp. 460–76.

6 Morgan, J. J., *American Gas Practice,* Vol. 1, Jerome J. Morgan, Maplewood, N. J., 1931, pp. 714–44, 773–7.

7 Gluud, W., and Jacobson, D. L., *International Handbook of the By-Product Coke Industry,* Chemical Catalog Co., New York, 1932, pp. 672–5. Pacific Coast Gas Association, *Gas Engineers' Handbook,* McGraw-Hill Book Co., New York, 1934, pp. 447–53.

8 Sperr, F. W., Jr., *Recent Progress in Science in Relation to the Gas Industry,* American Gas Association, New York, 1926, Chapter XI.

9 Jacobson, D. L., and Carvlin, G. M., *Proc. Am. Gas Assoc.,* 1932, 1028–9.

10 Powell, A. R., *Selective Removal of Liquid-Phase Gum-Formers and Naphthalene by Oil Scrubbing,* American Gas Association, New York, 1935.

11 Schwarz, S. C., *Proc. Pacific Coast Gas Assoc.,* 18, 290–300 (1927).

12 Haug, J. S., *Proc. Am. Gas Assoc.,* 1926, 1165–78.

of the "shock" method of condensation for removal of naphthalene has been borne out in practice at a small gas plant [13] and by other more extensive tests made with different speeds of condensation.[14]

In coal-gas manufacture, it is quite common practice to secure final cooling of the gas by direct contact with water. Usually this water is recirculated, being recooled before entering the final gas cooler by contact with flowing air in a cooling tower. The condensed naphthalene comes to the surface of this water as a scum and is usually skimmed off the surface as the water rests in a sump. The circulating cooling water may be kept in a much more naphthalene-free condition by washing it with some naphthalene solvent, such as certain oils or tar, before the water enters the cooling tower.[15]

In addition to the normal condensation operations in coal-gas manufacture, various proposals and attempts have been made to apply low-temperature cooling to the gas, not only for more complete removal of naphthalene but also for removal of other constituents. One of the most complete and recent of these developments is the Lenze process. The theory and experimental data related to this process were described in 1926,[16] and several years later more complete descriptions of the process, including operating data from several plants in Europe, were published.[17]

In the Lenze process, coal gas is freed of the larger portion of its content of naphthalene, water vapor, tar, and ammonia by washing with a spray of 4 to 6 percent ammonia liquor cooled to 0 to −5° C. This is followed by a water wash of the gas at 0° C. One of the features of the Lenze process is that the necessary refrigeration for carrying on the process is secured by utilizing waste heat, such as the sensible and latent heat of the hot coal gas leaving the carbonization chambers. By this process the naphthalene content of the gas is reduced to about 2 grains per 100 cubic feet. Several detailed descriptions of the Lenze and similar processes have been published, including a description of the installation at Mainz,[18] the installation at Wurzburg,[19] and another plant that combines pressure with the refrigeration primarily for the recovery of light oil.[20]

Absorption by solvents in a washer or scrubber is by far the most common commercial method for naphthalene removal, especially in America and England. It lends itself easily to positive control of the naphthalene content of the send-out gas, practically no attention or labor is required, and the equipment is most economical in operation.

Where light oil is recovered from coal gas by washing with a solvent oil, such as petroleum wash oil or a tar oil, there is a considerable incidental removal of naphthalene. This will not be discussed here since the subject of light-oil removal is covered in Chapter 28. However, in many coal-gas plants efficient removal of naphthalene is sought either with or without recovery of light oil, and this requires a technique of scrubbing quite different from that used for light oil.

The theory involved in the absorption of naphthalene from gas by the use of sol-

[13] Sebald, H. A., *Gas Age-Record*, **50**, 875 (1922).

[14] Prater, T. H., *Gas J.*, **173**, 544–7 (1926).

[15] Heinrich Koppers A.-G., Brit. Pats. 336,484 (1929); 357,801 (1930).

[16] Lenze, F., and Rettenmaier, A., *Gas- u. Wasserfach*, **69**, 689–91 (1926).

[17] Lenze, F., and Rettenmaier, A., *ibid.*, **74**, 1169–72 (1931); *Gas J.*, **197**, 139–42 (1932).

[18] Pippig, H., *Gas- u. Wasserfach.*, **77**, 346–9 (1934).

[19] Schon, E., *ibid.*, **81**, 870–7 (1938).

[20] Wucherer, J., *ibid.*, **78**, 118–21 (1935).

vents has been quite extensively discussed in several publications. One of the most extensive studies of this matter has been made by Spelce,[21] who not only discussed the matter of equilibrium relationships in the absorption of naphthalene by petroleum oils but also gave the results of tests on velocity of absorption with packed towers, bubble-cap columns, etc. Powell[10] also discussed in some detail the theoretical considerations involved in removal of naphthalene from gas by solvents, with special emphasis on selectivity of removal in the presence of various light-oil hydrocarbons. Morgan[6] gave a good résumé of the theoretical principles of naphthalene absorption by solvents.

In general, absorption of naphthalene from gas by solvent oils requires contacting of the gas with a very small quantity of the oil. Whereas absorption of light oil requires 10 to 15 gallons of wash oil per 1,000 cubic feet of gas, efficient absorption of naphthalene requires only 0.01 to 0.10 gallon per 1,000 cubic feet. In fact, where the selective absorption of naphthalene is required in the presence of light-oil vapor in the gas, it is quite necessary to limit the amount of solvent oil very carefully in order to avoid loss in heating value of the gas due to incidental absorption of the light oil. This requires a scrubber of special design in order to contact a large quantity of gas with a small quantity of oil efficiently and at the same time secure the necessary countercurrent flow of oil with regard to gas flow.

Various commercial types of naphthalene scrubbers are described in textbooks.[5, 6, 7] In America, vertical towers of various designs have been used almost entirely.

The Koppers naphthalene scrubber,[6, 7,]

[10, 22] has found extensive use over a long period of years. Figure 1 is a diagrammatic view of this scrubber. The gas first passes through the lower half of a tall packed tower where it contacts partially spent oil that is recirculated through this part of the tower at a rather high rate of recirculation; here the naphthalene content of the gas is considerably reduced. The gas then passes through the upper half of the tower where it contacts a relatively small volume of fresh oil injected at the top through sprays. This fresh oil is added at so low a rate that it cannot be sprayed continuously to secure good contact between gas and oil, and is, therefore, added in "shots," that is, injected periodically at rates high enough to thoroughly wet the packing in the fresh-oil section of the tower. The contact with the fresh oil reduces the naphthalene content of the gas to an amount acceptable for distribution purposes. After the fresh oil has passed through the fresh-oil section, it joins the large volume of recirculating oil and thereby continuously refreshes this batch of oil. Periodically, the spent oil is withdrawn from the recirculating oil system, to be disposed of in any of several ways to be mentioned later. A typical Koppers naphthalene scrubber is shown in Fig. 2.

That this type of scrubber is very selective in its absorption of naphthalene when light-oil vapors are also present in the gas has been shown by Kohr.[23] Operation of the scrubber over a long period of time indicated an average loss in heating value of the gas of considerably less than 1 Btu per cubic foot, whereas during this same period almost complete removal of naphthalene had been secured.

[21] Spelce, J. E., *Proc. Pacific Coast Gas Assoc.*, **16**, 345–85 (1925).

[22] Powell, A. R., Merritt, M., and Byrne, J. F., *Gas Age-Record*, **60**, 3–4, 8, 12 (1927). Smith, C. J., *Am. Gas J.*, **148**, No. 5, 49–51 (1938).

[23] Kohr, A. A., *Gas Age-Record*, **57**, 187–8 (1926).

Another type of scrubber that has been used in America for the removal of naphthalene from coal gas and other manufactured gas is the Feld scrubber. Descriptions of some of these installations together with operating results were given some

America, but there are few if any references in the literature to them. Some gas plants have improvised crude naphthalene scrubbers from towers built for other purposes but the amount of oil required is always higher than it should be for efficient opera-
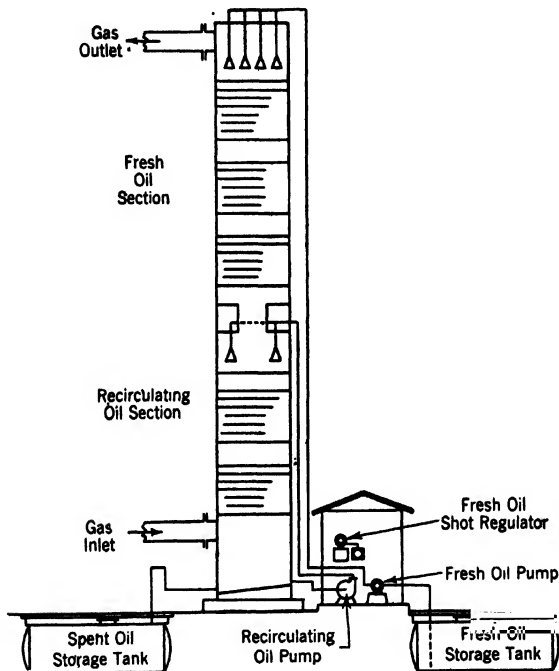
FIG. 1. Diagrammatic view of Koppers naphthalene scrubber.

years ago.[24] Briefly, the Feld scrubber consists of a vertical tower inside of which are a series of revolving cones attached to a shaft in the center. The oil flows downward from cone to cone, being thrown into a spray by each revolving cone. The gas passes up countercurrent to the flow of oil.

Several other types of naphthalene scrubbers have been used to a limited extent in

[24] Anon., *ibid.*, **57**, 878 (1926). Terry, H. W., Jr., *ibid.*, **59**, 743-7 (1927).

tion, and loss of heating value of the gas is high.

In Europe, many types of naphthalene scrubbers have been developed and are in successful operation. Schwarz[11] gave an excellent review of European naphthalene scrubbers as well as some American scrubbers. The Holmes rotary brush washer has been very popular in England for removing naphthalene from coal gas. This equipment consists of a horizontal cylindrical

Fig. 2. A typical Koppers naphthalene scrubber (the single tower in foreground).

shell divided into different chambers along its length. Through the center is a shaft to which are attached brushes that revolve very slowly. Oil flows into the chamber at one end and thence slowly flows from chamber to chamber until it reaches the other end. The revolving brushes are wetted by the oil in the bottom of each chamber and secure contact between oil and gas, the gas flowing through each chamber in series countercurrent to the oil. Other types of horizontal rotary washers used in England are the "Whessoe" and the "Standard." The characteristic of all these types of naphthalene scrubbers that causes them to be efficient is their ability to contact large volumes of gas with small volumes of oil in a countercurrent manner.

One rather novel method of naphthalene removal used to some extent in Germany may be mentioned here, although its nature places it nearer the next group of processes, namely, injection of a solvent into the gas-distribution system. In this process, the gas is saturated with the vapor of a naphthalene solvent, for example, tetralin, as the gas leaves the compressor at a somewhat elevated temperature. When this hot gas passes through the after-cooler, the solvent is condensed and carries along with it most of the naphthalene originally present in the gas.[25] The condensate is recirculated back to be revaporized and periodically is regenerated so as to separate the naphthalene.

The solvent oil used in naphthalene scrubbers not only must be a naphthalene solvent but also must have a low vapor pressure to prevent excessive loss by vaporization, must not be too viscous to prevent good distribution and contact with the gas, and must be relatively low in price. In America, petroleum oils are used almost exclusively. When properly chosen, they possess all the above advantages and have the added advantage of being absolutely free of naphthalene before use. Petroleum oils of widely varying characteristics are suitable for this purpose, the chief requirement being that the oil be fluid enough at ordinary temperature to permit ease of handling and good contact with the gas.

In many instances, especially where carburetted water gas is produced at the same plant as the coal gas, ordinary gas oil may be used, provided that it is not too viscous. The spent gas oil from the naphthalene scrubber may then be added to fresh oil for the purpose of carburetting the water gas. By this system of operation the naphthalene content of the water gas is not increased since the gas cooling system removes the excess of naphthalene.[6] The amount of gas oil required for removal of naphthalene from coal gas averages only about 0.05 gallon per 1,000 cubic feet, whereas about 3 gallons per 1,000 cubic feet of gas oil is used for carburetting water gas, so that ordinarily the percentage of spent naphthalene scrubber oil added to the fresh carburetting oil is quite small. In America, this practice is quite common, and even in England it has been followed to some extent and the spent gas oil has been found satisfactory in water-gas sets.[26]

In some plants, it has proved more convenient or economical to regenerate the spent naphthalene scrubber oil for reuse in the scrubber. Green[27] has given a very complete description of removal of naphthalene and gum-forming hydrocarbons at a plant where the spent gas oil is regenerated by distillation.

In Europe, tar oils are much more com-

25 Michaelis, P., *Glückauf,* **72,** 1102–7 (1936). Oppelt, W., *ibid.,* **74,** 503–7 (1938).

26 Richardson, B., *Gas J.,* **161, 384** (1923), 162, 348–50 (1923).

27 Green, S., *Proc. Am. Gas Assoc.,* **1939,** 573–85.

mon than petroleum oils for absorption of naphthalene from coal gas. Tar oils may be of the nature of creosote oil but are more commonly the higher-boiling anthracene oils. They possess the advantage over petroleum oils of being able to absorb more naphthalene before becoming spent, but they have the disadvantages of not being entirely free of naphthalene before use and of solidifying rather readily at low temperatures.

It has long been recognized that it is quite difficult to obtain tar oils that are sufficiently free of naphthalene to give efficient removal when used as absorbents for removing naphthalene from coal gas.[28] Naphthalene-free creosote has proved somewhat satisfactory, but care is necessary with anthracene oils since they may solidify.[26] Cooper[29] has described English practice in the use of anthracene oil for removal of naphthalene from coal gas and also the stripping of the spent oil by distillation for reuse.

The application of solvents, either in liquid or vapor form, to the gas-distribution mains is in reality a method that utilizes the lines of the gas-distribution system as the naphthalene scrubber. However, since the contacting of the gas and the solvent is not countercurrent in principle, the amount of solvent required is greater than in a properly designed scrubber. Also, the naphthalene content of the gas is not subject to as close control as it is in a scrubber located in the gas plant.

The practice of solvent injection up to about 1927 has been reviewed briefly by Schwarz.[11] Petroleum oils are commonly used in America where solvent injection is practiced. The amount of oil varies between 9 and 25 gallons per million cubic feet, and with this quantity of oil naphthalene is likely to condense at the ends of the lines in cold weather.[30] Blake[31] has compared the results obtained by spraying oils of various boiling ranges. A mixture of petroleum distillate and gas oil was found to be the most efficient.

European practice in solvent injection has been discussed by Meade.[5] In addition to being sprayed in the form of a mist, oil may be introduced into the gas stream as a vapor. Although tar oils are widely used in Europe, preference is shown for light paraffin oils such as kerosene. In his review of the subject, Meade gave some of the details of the equipment for spraying and also for the other process of vaporizing solvent into the lines.

One of the more recent solvents employed rather extensively in Europe but only to a very limited extent in America is tetralin. Shea[32] has presented a review of tetralin injection for the prevention of naphthalene deposits and some experiences in one American gas company's distribution system. He says that European companies claim that the cost of tetralin for this purpose varies between 0.07 and 0.14 cent per 1,000 cubic feet of gas treated. Since tetralin has a relatively high vapor pressure, a considerable portion of the injected tetralin simply carries on as a vapor with the gas, and this portion has no value as far as naphthalene removal is concerned. A list of further references on tetralin was given by Shea.

Adsorption by solids for removing naphthalene is of relatively little importance

28 Schweizer, W., *J. Gas Lighting*, **122**, 97 (1913).

29 Cooper, C., *Gas World*, **108**, No. 2796, Coking Sect., 27–31 (1938).

30 Kowalke, O. L., and Pesch, A. W., *Gas Age-Record*, **49**, 433–5 (1922); *Am. Gas J.*, **116**, 347–9, 354–5 (1922).

31 Blake, T. V., *Gas J.*, **177**, 749–50 (1927).

32 Shea, M. E., *Gas Age-Record*, **81**, No. 8, 23–5, 34, 40 (1938); *Am. Gas J.*, **148**, No. 4, 31–4, 53 (1938).

since cheaper and more convenient methods are available, especially where removal of naphthalene is desired independently of the recovery of light oil from the coal gas.

In some plants in Continental Europe where light oil is recovered from coal gas by the active charcoal process, naphthalene is simultaneously removed.[33] However, in England, naphthalene is first removed from the coal gas by oil washing before the gas is contacted with the active charcoal for recovery of light oil.[34]

A German investigation determined the effectiveness of silica gel as a means of removing naphthalene from coal gas along with the coincident dehydration of the gas.[35] Complete removal of naphthalene was secured. One rather interesting process, probably of little commercial value, is described in an Austrian patent,[36] in which the coal gas is contacted with rubber, for example comminuted rubber from old tires, whereby naphthalene is removed from the gas; regeneration is secured by agitation of the spent rubber in a current of air or steam, or merely by exposure to the air.

REMOVAL OF INDENE, STYRENE, ETC.

Indene and styrene are liquid unsaturated hydrocarbons that occur in the vapor state as minor constituents of coal gas. They are more or less completely removed from coal gas in the recovery of light oil, and reference should be made to Chapter 28 for a more detailed description.

The presence of these hydrocarbons in manufactured gas first attracted attention by their tendency to polymerize and form "liquid-phase" gum in distribution systems, when they condensed from the gas as "drip oil" or condensate.[37] Although these compounds occur in coal gas in substantially as great quantities as in carburetted water gas, only the latter gas ordinarily gives trouble due to liquid-phase gum, since coal gas is relatively dry as far as condensation of oil is concerned, and indene and styrene polymerize only when in solution in a liquid phase and are harmless in the vapor state. However, it is sometimes desired to remove indene and styrene from coal gas independently of light-oil removal, especially when the coal gas is later to be mixed with carburetted water gas.

Some years ago a very complete description of this subject was given by Fulweiler and his colleagues, together with references to publications up to that time.[38] Later published papers, including descriptions of processes and plants for the removal of the "liquid-phase gum-formers" from gas, have been summarized by Powell.[39]

Tests that have been made on coal gas from various sources show styrene contents ranging from 0.002 to 0.006 percent by volume, and indene contents ranging from 0.004 to 0.013 percent by volume.[38] From what has been said previously, it is quite impossible to make any general statement as to what percentage of these compounds should be removed from the coal gas to satisfy all conditions. Usually, removal is not required at all.

Brown [37] has pointed out that close control of the oxygen content of gas is helpful in preventing liquid-phase gum formation, even when the indene and styrene are

[33] Engelhardt, A., and Rüping, H., *Gas- u. Wasserfach*, **76**, 478–84 (1933). Simon, A., *ibid.*, **79**, 357–62 (1936).

[34] Hollings, H., and Hay, S., *Chemistry & Industry*, **1934**, 143–55; *Gas World*, **100**, 189–93 (1934).

[35] Brückner, H., and Ludewig, W., *Gas- u. Wasserfach*, **78**, 459–62 (1935).

[36] Nottes, G., Austrian Pat. 143,810 (1935).

[37] Brown, R. L., *Proc. Am. Gas Assoc.*, **1924**, 1353–1411.

[38] Ward, A. L., Jordan, C. W., and Fulweiler, W. H., (*a*) *Ind. Eng. Chem.*, **24**, 969–77, 1238–47 (1932); (*b*) *ibid.*, **25**, 1224–34 (1933).

[39] Powell, A. R., *Proc. Am. Gas Assoc.*, **1938**, 577–92.

not removed at all. Refrigeration or compression of the gas has been suggested and applied for the purpose of decreasing the indene and styrene content of gas.[39]

However, where removal of indene and styrene from gas is necessary, scrubbing of the gas by oil is probably the simplest and commonest method.[10, 27] The equipment and the general method of operation are almost identical to those for removal of naphthalene, with the single exception that a greater volume of fresh scrubbing oil must be fed to the scrubber. Thus, whereas naphthalene removal requires only 0.01 to 0.10 gallon of fresh-oil feed per 1,000 cubic feet of gas, efficient removal of the liquid-phase gum-formers calls for 0.10 to 0.50 gallon per 1,000 cubic feet. However, this volume of oil is considerably lower than the 15 gallons per 1,000 cubic feet generally used for recovery of light oil from gas, and the result is that the removal of the indene and styrene is relatively selective, only a minor portion of the nongum-forming hydrocarbons being absorbed from the gas.

REMOVAL OF ETHYLENE

A very considerable amount of experimental work has been carried on with the objective of removing ethylene from coal gas and other manufactured gas, thereby converting it into a useful byproduct. The recovery of a useful byproduct is the only objective, since ethylene is not a harmful constituent of the coal gas but, on the contrary, contributes quite materially to the heating value of the gas when used as a fuel.

Some commercial application has been made of the removed ethylene in Europe, but in America such processes have been used only sporadically and on relatively small volumes of coal gas. A very excellent and complete review of this subject up to the year 1926 has been made by Curtis.[40]

As has been pointed out in another chapter, ethylene, C_2H_4, occurs in normal coal gas to the extent of about 2.5 percent by volume. Other olefin hydrocarbons, such as propylene and the butylenes, are also present, but in much smaller quantities.

Systems that have been used or proposed for recovery of ethylene from coal gas are: (1) direct absorption from coal gas by (a) sulfuric acid, (b) active charcoal, and (c) other absorbents; and (2) concentration by fractional liquefaction or fractional distillation at low temperatures, with or without subsequent absorption, by (a) the Claude process, (b) the Linde process, and (c) other processes.

Applying the well-known principle of absorption of ethylene by concentrated sulfuric acid, a process for the recovery of ethylene in the form of ether from coal gas was patented in 1896.[41] This process was tried out at Richmond, Va., in 1900, without commercial success.

Bury and Ollander[42] operated a semicommercial plant in England during World War I in which coal gas containing 2 percent of ethylene by volume was treated with 95 percent sulfuric acid and ethyl alcohol was recovered as a byproduct. The coal gas was first purified by the usual means and was then dried by contact with 80 percent sulfuric acid before being treated with the 95 percent acid. With an absorption temperature of 70 to 80° C, 70 percent of the ethylene was removed from the gas and a 70 percent conversion of

40 Curtis, H. A., *Recent Progress in Science in Relation to the Gas Industry*, American Gas Association, New York, 1926, Chapter X.

41 Fritzsche, P., Brit. Pat. 20,225 (1896).

42 Bury, E., and Ollander, O., *Gas J.*, **148**, 718–21 (1919); *Chem. Trade J.*, **66**, 36–7, 61–2 (1919); *Iron & Coal Trades Rev.*, **99**, 804–5, 831–2 (1919). Bury, E., *Gas World*, **73**, 123–5 (1920); *Gas J.*, **151**, 449–50 (1920).

this recovered ethylene could be realized into ethyl alcohol, giving a yield of 1.6 gallons of alcohol per ton of coal carbonized. A considerable amount of sulfur dioxide was released during the absorption, which made a problem of its removal and utilization or disposal.

The effects of temperature, pressure, water vapor, contact surface, etc., were extensively discussed and much experimental work was done prior to 1925,[43, 44, 45] whereas interest in the direct absorption of ethylene from coal gas appears to have almost ceased in more recent years.

The rather sluggish absorption of the ethylene by sulfuric acid may be catalyzed by many substances, but other substances inhibit the absorption. De Loisy[46] showed that mercury with vanadic acid, uranic acid, or molybdic acid is a catalyst. De Loisy and Damiens[44] named cuprous compounds as catalysts. Lommel and Engelhardt[47] have demonstrated that silver sulfate is an excellent catalyst, as have also Gluud and Schneider,[48] who further discovered lead, iron, and calcium sulfate to be catalysts. Two British patents[49] describe the addition of compounds of osmium, iridium, platinum, palladium, and other rare metals, as well as various compounds of copper, iron, cobalt, and nickel to catalyze the absorption of ethylene by sulfuric acid. Hickson and Bailey[50] stated that the absorption of ethylene by sulfuric acid is inhibited by naphthalene, phenol, m-cresol, pyridine, and other substances that may be present in coal gas in small quantities.

The recovery of ethyl alcohol from coal gas by means of the absorption of ethylene directly from the gas by sulfuric acid is probably not economically feasible except under most unusual conditions. Furness[51] has discussed this matter from the standpoint of English conditions, and a discussion from the standpoint of American conditions[52] has also been published.

Although most of the schemes for absorbing ethylene directly from coal gas have centered around the use of sulfuric acid, activated charcoal has been proposed or used.[53] Curme has patented the use of acetone[54] and of mercuric sulfate solution.[55] Several other absorbents for ethylene have been proposed, but mostly for refinery or other gases that may be relatively high in ethylene content or under high pressures. None of these processes is now in commercial use for recovery of ethylene from coal gas in America, as far as is known.

Of considerably more practical importance than the direct absorption of ethylene from coal gas has been the recovery of ethylene as a liquefied product in conjunc-

[43] Plant, S. G. P., and Sidgwick, N. V., *J. Soc. Chem. Ind.*, **40**, 14–8T (1921). Thau, A., and Bertelsmann, W., *Glückauf*, **57**, 189–94, 221–5 (1921). Tidman, C. F., *Iron & Coal Trades Rev.*, **102**, 350 (1921). Neumann, B., *Gas- u. Wasserfach*, **67**, 1–3, 14–6, 53–5 (1924).

[44] Damiens, A., *Compt. rend.*, **175**, 585–8 (1922). De Loisy, E., and Damiens, A., *Chimie & industrie*, Spec. No., May, 1923, pp. 664–70.

[45] Gluud, W., Keller, K., and Schneider, G., *Ber. Ges. Kohlentech.*, **1923**, 224–31.

[46] De Loisy, E., *Compt. rend.*, **170**, 50–3 (1920).

[47] Lommel, W., and Engelhardt, R., *Ber.*, **57B**, 848 (1924).

[48] Gluud, W., and Schneider, G., *ibid.*, **57B**, 254–5 (1924).

[49] N.-V. de Bataafsche Petroleum Maatschappij, Brit. Pats. 336,608, 336,633 (1929).

[50] Hickson, Wm. S. E., and Bailey, K. C., *Sci. Proc. Roy. Dublin Soc.*, **20**, 267–79 (1932).

[51] Furness, R., *Ind. Chemist*, **1**, 475–80 (1925).

[52] Anon., *Gas Age-Record*, **50**, 411–4 (1922).

[53] T. Goldschmidt A.-G., Brit. Pat. 146,332 (1920). Johnson, J. Y., Brit. Pat. 190,203 (1921). Soddy, F., U. S. Pats. 1,422,007–8 (1922). Engelhardt, A., *Glückauf*, **73**, 925–33 (1937).

[54] Curme, G. O., Jr., U. S. Pat. 1,422,184 (1922).

[55] Curme, G. O., Jr., U. S. Pat. 1,315,541 (1919).

tion with the preparation of hydrogen from coke-oven gas by compression and refrigeration. The preparation of hydrogen from coke-oven gas will be discussed in the next section of this chapter, but at this point the processes will be described since ethylene is one of the products separated during this hydrogen preparation. In general, two systems have been developed for the separation of coal-gas constituents by compression and refrigeration—the Claude system and the Linde system. Although both have been considerably modified, the basic difference between these systems is in the method of obtaining the cooling effect.

The Claude system [56] compresses the coal gas, after preliminary purification, to 30 or 40 atmospheres, and then causes this gas to expand in a heat engine and do external work. The expansion of the gas in the heat engine or "hydrogen motor," as it is called by Claude, causes a decided cooling of the gas, the accumulated effect eventually resulting in partial liquefaction of the coal gas.

In contrast to the external heat engine of Claude, Linde [57] secures the cooling effect by internal expansion of the compressed gas, thereby utilizing the well-known Joule-Thomson effect. The coal gas, after preliminary purification, is compressed to pressures ranging from 10 to 200 atmospheres and is then expanded to atmospheric pressure without performing external work. The cooling effect is made cumulative by means of heat exchangers, and finally partial liquefaction of the coal gas results.

The Claude process has been in commercial operation on coke-oven gas in French mining regions for the production of hydro-gen.[58] After removal of light oil, the gas was compressed to 25 atmospheres and then scrubbed with oil to debenzolize further. It was further scrubbed with water and lime water to remove carbon dioxide. The gas then entered the liquefying apparatus, where it was progressively cooled by the principle mentioned earlier. A fraction rich in ethylene was first to liquefy, followed at lower temperatures by other fractions, and finally hydrogen was left in a gaseous state, largely purified of the other constituents of the coal gas. Scott [59] has described the Bethune plant in France, where the treatment of the ethylene fraction with sulfuric acid results in the production of 200 kilograms of ethyl alcohol per ton of ammonia produced from the hydrogen.

The Linde process has apparently found more extended commercial use in Europe than the Claude process, at least in recent years. Borchardt [60] has described the Linde system in great detail, giving complete analyses of the various liquefied fractions and also cost data.

Pallemaerts [61] has described in a very thorough manner the application of the Linde process to the production of hydrogen from coke-oven gas in a Belgian plant which used the hydrogen for ammonia synthesis. After the usual preliminary purification (light oil, carbon dioxide, etc.) the gas was compressed and cooled. The first fraction separates at 120° K (−153° C), and this fraction was called "ethylene." Its composition was as follows:

[56] Claude, G., *J. Ind. Eng. Chem.*, **14**, 1118-9 (1922); *Engineering*, **114**, 506-7 (1922).

[57] Pollitzer, F., *Z. Ver. deut. Ing.*, **56**, 1540-6 (1912). Linde, F., *Z. angew. Chem.*, **26**, 814 (1913).

[58] Curtis, H. A., *Fixed Nitrogen*, Chemical Catalog Co., New York, 1932, pp. 212-5.

[59] Scott, E. K., *Colliery Guardian*, **127**, 737 (1924).

[60] Borchardt, P., *Gas- u. Wasserfach*, **70**, 562-8 (1927).

[61] Pallemaerts, F. A. F., *Proc. Second Intern. Conf. Bituminous Coal*, **2**, 178-201 (1928); *Chem. & Met. Eng.*, **35**, 741-4 (1928).

	PERCENT
C$_2$H$_4$	30.6
C$_3$H$_6$	6.1
C$_2$H$_6$	30.6
CH$_4$	30.6
CO	2.0

This ethylene fraction was further concentrated by fractional distillation into a product containing 80 to 95 percent ethylene, or else was treated directly with sulfuric acid to produce ethyl alcohol or ether.

Bronn [62] has described the application of the Linde process to separation of the constituents of coke-oven gas at the plant of Concordia Bergbau A.-G. at Oberhausen, Germany. This paper includes the complete layout of the plant and the analyses of the raw gas, the intermediate and finished products, etc.

Gluud and Schneider [63] have described a process especially designed for the recovery of ethylene in the form of ethyl alcohol from coke-oven gas that utilizes the fractional condensation system of Linde or its equivalent. The gas was purified of carbon dioxide, etc., in the regular manner, and the liquefaction was then so conducted that a fraction containing 70 percent ethylene was obtained. This ethylene-rich fraction was given a preliminary wash with concentrated sulfuric acid, the sulfur dioxide thus formed was removed, and then there was a final absorption in concentrated sulfuric acid containing silver sulfate as a catalyst. The catalyst was then removed, the acid diluted with water, and the ethyl alcohol distilled out. Laboratory experimental data were given, as well as estimates of the economics of the process.

Another modification of the liquefaction method for recovery of ethylene from coal gas operates on the principle of total liquefaction of hydrocarbons in the gas followed by fractional distillation to separate the ethylene and other hydrocarbons.[64]

REMOVAL OF HYDROGEN

Like ethylene, hydrogen may be recovered from coal gas for the purpose of serving as a useful product, and, like ethylene, the hydrogen is recovered by the general principle of compression and refrigeration. In fact, the primary purpose in separating coal gas into its various constituents is usually the recovery of hydrogen, and the coincident recovery of ethylene, etc., is more or less secondary.

The hydrogen recovered from coal gas is used for various hydrogenation processes and for the manufacture of synthetic chemicals. In America very little, if any, hydrogen is recovered from coal gas, but in Europe coal gas is not an uncommon source of hydrogen for the synthetic-ammonia industry and various hydrogenation industries. Curtis [58] stated that 23 percent of the hydrogen used for ammonia synthesis was obtained from coke-oven gas by the liquefaction separation.

In the previous section on ethylene recovery, reference has been made to the two general commercial systems for recovery of hydrogen from coal gas, namely, that of Claude and that of Linde. The fractional separation leading up to the recovery of more or less pure hydrogen involves further details of operation.

One of the best descriptions of a plant recovering hydrogen from coke-oven gas for the manufacture of synthetic ammonia has been given by Pallemaerts.[61] The plant was that of the Union chimique Belge at Ostend, Belgium, which used the Linde

[62] Bronn, J., *Z. angew. Chem.*, **42**, 760–8 (1929).

[63] Gluud, W., and Schneider, G., *Gas- u. Wasserfach*, **70**, 97–102 (1927).

[64] Bronn, J., *Z. kompr. flüss. Gase*, **25**, 53–7, 78–81, 93–7 (1926). Sakmin, P. K., *ibid.*, **32**, 1–5, 13–15 (1936).

system for the separation of the hydrogen from the coke-oven gas. The preliminary treatment of the gas at this plant was somewhat different from that at other plants. Whereas other plants remove carbon dioxide with a water wash while the gas is under pressure, the plant at Ostend removed both hydrogen sulfide and carbon dioxide by an ammonia wash process with the gas at atmospheric pressure. This treatment reduced the carbon dioxide to less than 0.1 percent. This was followed by a water wash and a sulfuric acid wash to remove ammonia, and finally by a caustic soda wash to remove the small remaining amount of carbon dioxide and dry the gas. The gas was then compressed to 9 atmospheres, refrigerated by liquid ammonia, and warmed to normal temperature by a cold exchanger. The compressed gas was washed with water, using a little over 1 volume of water per volume of compressed gas. The main object of this water wash was to remove acetylene. The purified coke-oven gas was then cooled for a second time by means of cold exchangers and ammonia refrigerators to a temperature of $-45°$ C. This removed the majority of the water vapor. Then the cold compressed gas entered the fractionation apparatus where the final cooling was obtained from the Joule-Thomson effect of the expansion of compressed gases that had passed through the refrigeration cycle and had been separated. Three liquid fractions were separated out in the fractionating apparatus, an "ethylene" fraction, a "methane" fraction, and a "carbon monoxide" fraction which had the composition shown in Table II.

After the condensation of the fractions shown in Table II, the compressed cold gas comprised a mixture of hydrogen and nitrogen, containing small amounts of methane and carbon monoxide. These impurities

TABLE II

COMPOSITION OF FRACTIONS OBTAINED BY THE LINDE SYSTEM IN SEPARATION OF HYDROGEN FROM COKE-OVEN GAS [61]

	Ethylene Fraction	Methane Fraction	Carbon Monoxide Fraction
Condensation			
°K	120	85 to 95	Below 85
°C	-153	-178 to -188	Below -188
Composition, Percent by Volume, Gaseous State			
Methane	30.6	74.4	6.9
Ethane	30.6	....	....
Ethylene	30.6	1.9	....
Propane	6.1	....	....
Carbon monoxide	2.0	9.6	18.0
Oxygen	. .	1.2	2.0
Hydrogen	....	4.2	....
Nitrogen	....	8.7	73.1

were practically completely removed by washing the cold compressed gas with liquid nitrogen which completely removed the methane and reduced the carbon monoxide to 0.001 percent by volume. During this liquid-nitrogen wash the conditions were regulated to give a mixture of hydrogen and nitrogen containing 3 moles of hydrogen per mole of nitrogen. The reason for this was, of course, that this is the composition needed for synthesis of ammonia, NH_3. For other purposes, the presence of nitrogen might be disadvantageous, and in such cases it would be necessary to modify the process somewhat to give as low a content of nitrogen in the finished hydrogen as possible.

The various gases separated in the fractionating apparatus may, after expansion, be used as fuel or may be recovered as useful byproducts. The recovery of ethylene in connection with coal-gas liquefaction has been described in the preceding section of this chapter.

Various other descriptions of hydrogen-recovery processes and plants have been

referred to in the preceding section on ethylene.[56, 57, 59, 60, 62, 64]

Fischer [65] has presented data showing the material and heat balances involved in the separation of hydrogen from coke-oven gas by compression and refrigeration. Also he has shown by means of tables and graphs the power requirements under different conditions of pressure and temperature.

Other schemes that do not depend on fractional liquefaction of the coal gas have been suggested for the separation and recovery of hydrogen. One such scheme has been suggested by Hofsäss.[66] The coal gas is compressed to 90 atmospheres, and under these conditions the hydrogen is absorbed by molten potassium or sodium. By heating, the hydrogen is evolved and the metal regenerated for further use.

In addition to processes for recovering the elemental hydrogen in coal gas, many others have been developed for cracking the hydrocarbons in coal gas to produce more hydrogen, and still others make use of the reaction of steam with hydrocarbons to produce hydrogen and carbon dioxide. These chemical conversions of coal gas will not be considered here.

REMOVAL OF CARBON MONOXIDE

Since carbon monoxide is useful in contributing to the heating value of coal gas, and since this constituent gives no technical trouble in the distribution of the gas, its removal is exceptionally rare. In fact, in America there is no known plant that removes carbon monoxide from coal gas.

In Germany, however, a very extensive literature has sprung up on the removal of carbon monoxide for the purpose of rendering city gas nontoxic. Also several plants have been erected and are in operation for "Gasentgiftung." It should be stated, however, that the process has been mostly applied to mixtures of coal gas and water gas having relatively high contents of carbon monoxide rather than to straight coal gas, which normally contains only about 6 percent by volume. Schuster [67] described the entire subject of carbon monoxide removal in great detail, with references to the literature and pertinent patents, and later [68] he brought the subject up to 1939. The various processes for removing carbon monoxide from gas have been developed or put into commercial operation almost exclusively in Germany, very little having been done along these lines in other countries.

Although many methods for removing carbon monoxide from gas are available, all the actual commercial processes depend primarily on the reaction between carbon monoxide and water vapor to form hydrogen and carbon dioxide,

$$CO + H_2O = H_2 + CO_2$$
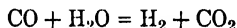
Schuster [67, 68] divided the processes into four classes, as follows: (1) conversion without removal of the carbon dioxide formed in the reaction; (2) conversion followed by removal of the carbon dioxide formed in the reaction; (3) conversion with simultaneous removal of the carbon dioxide formed in the reaction; and (4) conversion of the major part of the monoxide to the dioxide by water vapor followed by a second step consisting of the conversion of the remainder of the monoxide to methane by reaction with hydrogen.

Characteristic of the first class is the "Gesent" process of the Gesellschaft für

[65] Fischer, V., *Z. Ver. deut. Ing., Beiheft Folge,* 1937, 14–20, 1938, 110–1.
[66] Hofsäss, M., *Z. kompr. flüss. Gase,* 30, 13–14 (1933).

[67] Schuster, F., *Stadtgas-Entgiftung,* S. Hirzel, Leipzig, 1935, 167 pp.
[68] Schuster, F., *Handbuch der Gasindustrie,* R. Oldenbourg, Munich and Berlin, 1939, Vol. 3, Part 4.

Gasentgiftung of Berlin.[69, 70] In this process, the gas has added to it the proper amount of water vapor, is then heated in a heat exchanger, and finally flows into the contact chamber containing the catalyst for the conversion of the monoxide to the dioxide. The temperature in the contact chamber is about 400° C. The hot gas, with the carbon monoxide removed down to about 1 percent by volume, flows back through the heat exchanger and is finally cooled in a tower. It is claimed that a considerable proportion of the organic sulfur in the gas is converted into hydrogen sulfide during this conversion of monoxide to dioxide, and so the treated gas is finally passed through a dry purifier to remove this hydrogen sulfide. Since the carbon dioxide is not removed from the treated gas, the gas is somewhat diluted and its heating value reduced. For this reason, the gas before treatment should have a somewhat higher heating value than is desired for the final gas to be distributed to the city. This process was in operation at the gas plant at Hameln, Germany (about 350,000 cubic feet per day).

One representative of the second class of processes, that is, those involving the removal of the carbon dioxide from the gas after the conversion, is that of Müller.[71] The conversion is secured in the presence of iron oxide at a temperature of 500° C. After the conversion, the carbon dioxide that is formed is washed out of the gas by water under pressure or by potassium carbonate, etc. Another process based on somewhat the same general principle is the Nordhausen process.[72]

The third class of processes depends on using as a material in the conversion step a combination of a catalytic substance plus an absorbent for the carbon dioxide formed by the conversion reaction. A typical combination would be iron oxide plus lime or magnesia or both. When this material is saturated with carbon dioxide, it is then regenerated by heat, driving out the absorbed carbon dioxide and rendering the material suitable for further use. In these processes, the conversion temperature is approximately 500° C and the absorbent regeneration temperature is 800 to 900° C. Such a process was tested out on a pilot-plant scale by the Gesellschaft für Kohlentechnik.[73] A later development of a process of this type was that of Bössner and Marischka.[74] The mineral ankerite served as the contact material, since it contains iron, lime, and magnesia in the form of carbonates. As an alternative, an artificial mixture of these was used.

The fourth type of process, as mentioned before, consists of two steps: first the conversion of the largest part of the carbon monoxide by steam; and, second, the reduction of the remainder to methane by the reaction with hydrogen.[69, 75] Apparently this process is not in commercial operation and it has not as much chance of application to coal gas as it has to water gas, with its much higher content of carbon monoxide.[76]

[69] Mezger, R., *Gas- u. Wasserfach*, **78**, 573–9, 593–603 (1935).

[70] Gerdes, H. Ch., *ibid.*, **78**, 86–7 (1935). Schuster, F., *ibid.*, **79**, 450–4 (1936) ; *Z. Ver. deut. Ind.*, **81**, 143–6 (1937). Sander, A., *Chem.-Ztg.*, **60**, 33–6, 55–7 (1936).

[71] Müller, W. J., *Österr. Chem.-Ztg.*, **38**, 81–6 (1935). Wiener Gaswerke, *Gas- u. Wasserfach*, **75**, 507 (1932). Gerdes, H. Ch., Stief, F., and Plenz, F., *ibid.*, **80**, 493–5 (1937).

[72] Müller, H., *ibid.*, **81**, 590–9 (1938).

[73] Bestehorn, R., *Ber. Ges. Kohlentechnik (Dortmund-Eving)*, **3**, 306–62 (1930).

[74] Zahn, O., *Chem.-Ztg.*, **61**, 298–9, 458, 882 (1937) ; *Chem. Industries*, **41**, 40 (1937).

[75] Kemmer, H., *Gas- u. Wasserfach*, **72**, 744–51 (1929).

[76] Rosenthal, H., *ibid.*, **78**, 436–8 (1935).

Removal of Nitric Oxide

Nitric oxide, NO, has been recognized as a constituent of coal gas only during the last few years. Since the amount present seldom exceeds 0.0005 percent by volume, and is more typically only 0.000005 percent, this is easily understood.

This tiny amount of nitric oxide undergoes a reaction with oxygen and certain unsaturated hydrocarbons in the gas, forming nitrogenous or "vapor-phase" gum, which appears as a very fine fog or mist and remains suspended in the gas stream very persistently. When the gas containing this fine mist of gummy particles passes through a small orifice or changes direction of flow at high velocity, many of these gum particles are deposited and in time a stoppage results. This reaction proceeds rather slowly under ordinary conditions, and usually the gum particles do not appear in the gas stream for an hour or so after leaving the point of manufacture. This gummy mist in the gas affects the operation of many gas appliances, such as range lighters, pilot lights, and various automatic devices that include orifices or small passages for the gas; the amount is too small to cause stoppage of mains or service lines.

Since the chief source of nitric oxide in coal gas is the inleakage of flue gas and the pulling into the carbonization chamber of air during charging, etc., one of the obvious remedies for the trouble is the prevention of this contamination. Such precautions are often helpful, although it is seldom that troubles can be eliminated entirely by this attempt to cut off the nitric oxide at its source. Also, the removal from the gas of free oxygen would prevent trouble from this form of gum since oxygen is essential for its formation. Removal of oxygen from gas, however, is difficult and would involve considerable expense. Removal of the reactive hydrocarbons would also prevent formation of the gum, but usually this is not practicable because of the resultant loss in heating value of the gas, as well as for other reasons. In many cases, therefore, it is desirable to remove the nitric oxide from coal gas in order to prevent trouble from nitrogenous gum, and various processes have been proposed or used to accomplish this result.

One type of process that has proved to be quite efficient in large-scale operation over a period of years involves subjecting the gas to the action of an electrical brush discharge.[77] The apparatus, or "treater," for carrying out this process consists of rectangular chambers provided with series of plate electrodes arranged parallel to one another and only an inch or two apart. Each alternate electrode has protruding from it a large number of sharp-pointed pins. A high-tension alternating current is imposed on these electrodes so that there is a flow of electricity in the form of a brush discharge from the pointed electrodes to the plain plate electrodes. The gas flowing through the chambers is thereby highly ionized and a reaction is caused to take place that results in a transformation of the nitric oxide so that it can readily be removed from the gas in a subsequent scrubber. One installation of this electrical process has been treating about 24,000,000 cubic feet of coal gas per day since 1935, showing a nitric oxide removal efficiency of 97 to 98 percent. Another installation is now being made in a coal-gas plant of even greater capacity.

Another process for removal of nitric oxide involves the use of more or less fouled iron oxide, such as is employed for the re-

77 Shively, W. L., and Harlow, E. V., *Am. Gas Assoc., Prod. Conf. 1936; Trans. Electrochem. Soc.,* 69, 495–514 (1936).

moval of hydrogen sulfide from gas.[78] Since iron oxide is very often used for the purpose of purifying gas of hydrogen sulfide, some nitric oxide is always removed in such cases whether it is purposeful or not. The active material for absorption of the nitric oxide is iron sulfide, and so those boxes which are the most fouled from the standpoint of hydrogen sulfide removal are the most active for removal of nitric oxide. The first stage of this absorption appears to be physical adsorption followed by formation of complex ferronitrosyl sulfides or Roussin salts. Apparently this compound later reacts to form substances very similar to the nitrogenous gum. This type of process has been used to some extent in certain plants that are well provided with oxide box capacity and which are not subjected to high oxygen content of the gas or irregular conditions that tend to reverse the absorption of nitric oxide so that it would be released and sent out with the gas supply after first being absorbed.

Some experiments in England [79] have indicated removal of nitric oxide coincident with the catalytic removal of organic sulfur from coal gas. However, since the first announcement of this process there has been no published confirmation of successful commercial use.

REMOVAL OF WATER VAPOR

As was pointed out in a previous chapter, the water vapor present in coal gas is simply an inert and has no significant effect on the combustion of the gas, except as it may affect the flame temperature. However, coal gas leaving the point of manufacture is generally saturated with water vapor, and any decrease in temperature causes condensation of water in the gas-

distribution mains, which may lead to deposits that will cause stoppage of gas flow in the mains. The freeze-ups in exposed sections of pipe, where the condensed water is converted into ice, are examples. This trouble is relatively minor, however, compared to the effect of liquid water in promoting corrosion of gas mains; such corrosion constitutes a very appreciable item of expense in addition to causing stoppages.

Because of the harmful effects caused by the condensation of liquid water in gas-distribution systems, various commercial processes have been developed for the partial removal of water vapor before the gas leaves the manufacturing plant; these processes have been included under the general designation of "gas conditioning."

One of the earliest complete discussions of the subject of removal of water vapor from manufactured gas was by Sperr in 1926.[80] His classification of the methods available for removal of moisture from gas remains as valid today as it was at that time. He discussed the following four methods: (1) compression; (2) refrigeration; (3) treatment with hygroscopic substances; and (4) treatment with adsorbents.

Compression. When coal gas or any other gas is compressed and then cooled, water vapor condenses and the condensate may be removed. If this gas is then expanded to a lower pressure, it will be unsaturated with respect to water vapor. Although removal of water vapor is sometimes secured by this method as an incidental effect of compression of the gas for transmission purposes, it has found no application in the gas industry as a process having for its sole and specific objective the partial removal of moisture. The reasons are that the method is expensive

[78] Jordan, C. W., Ward, A. L., and Fulweiler, W. H., *Ind. Eng. Chem.*, **27**, 1180–90 (1935).

[79] Griffith, R. H., *Gas J.*, **220**, 480–2 (1937).

[80] Sperr, F. W., Jr., *Proc. Am. Gas Assoc.*, **1926**, 1250–73.

owing to cost of power for compression and that equally satisfactory and more economical methods are available. Some cost calculations made by Bragg [81] indicated a total cost of 0.91 cent per 1,000 cubic feet in winter and 0.58 cent in summer for the dehydration of coal gas by this scheme.

Refrigeration. If coal gas is cooled at the plant to a temperature somewhat lower than the lowest temperature encountered in the distribution system, the water dew point of the gas will be lowered to a point where no more condensation will occur. This method has been applied commercially for the partial removal of water from gas, either alone or in combination with the use of hygroscopic solutions. The theoretical considerations involved in this method have been given by Sperr.[80] The costs for this system applied to coal gas have been estimated by Bragg [81] as being 0.90 and 0.81 cent per 1,000 cubic feet for summer and winter conditions, respectively, when the compression system of refrigeration is used, and 0.74 and 0.66 cent per 1,000 cubic feet for summer and winter conditions, respectively, when the absorption system of refrigeration is used.

A rather novel system of partial gas dehydration by refrigeration in operation at Poughkeepsie, N. Y., has been described by Shively.[82] At this plant, water is cooled by means of vacuum pumps and the cooled water so produced is used in an indirect-type gas cooler to bring the dew point of the gas to a temperature lower than the lowest temperature of the gas-distribution system.

Treatment with Hygroscopic Substances. This method is by far the most popular for the partial removal of moisture from coal gas and other fuel gases, the reasons being the relatively low installation and operating costs, ease of control, and the wide range of hygroscopic substances that may be used. In general, the system comprises an absorber tower where the gas is contacted with a hygroscopic or water-absorbing solution, pumps for recirculating the absorbent solution through the tower, an evaporator for driving off the water absorbed by the solution, thereby regenerating it for further use, and various heat exchangers or coolers for the solution.

One of the most common absorbent liquids is a solution of calcium chloride. Bragg [81] has estimated the costs for this process as being 0.71 and 0.64 cent per 1,000 cubic feet, for summer and winter conditions, respectively. A description of the calcium chloride system has been given by Shively.[82] On the basis of several years of operating experience he gave the operating costs for this system as 0.40 to 0.48 cent per 1,000 cubic feet.

The partial dehydration of gas by sulfuric acid has also been proposed,[80] but as far as is known no commercial installations have yet been made. In England glycerin has been used for dehydration of gas in several plants.[83] Diethylene glycol has been employed as the absorbent liquid in several gas-dehydration plants in the United States, but only in those plants treating natural gas under pressure,[84] and it is not known to have yet been applied to coal gas.

Treatment with Adsorbents. In 1926, Sperr [80] discussed the possible use of silica gel as an adsorbent to partially dehydrate gas. Later, Shively [82] discussed not only silica gel but also activated alumina as adsorbents for water vapor from natural gas under high pressures. As far as is known, solid adsorbents have not been used for dehydration of coal gas.

[81] Bragg, G. A., *ibid.*, 1928, 1564–72.
[82] Shively, W. L., *ibid.*, 1939, 501–15.
[83] Tupholme, C. H. S., *Gas Age-Record*, 63, 311–3 (1929).
[84] Carson, H. J., *ibid.*, 82, No. 8, 17–8 (1938).

UTILIZATION OF COAL GAS

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Coal gas represents one of the more important fuel gases and as such has found wide and extensive application. The field of gas utilization involves many detailed and specific applications. Today, we recognize four main fields of service: residential, commercial, industrial, and chemical. In these fields coal gas is sold as a service that delivers energy in a convenient, flexible form that is ever ready. The residential field represents the use of coal gas in the home. The commercial field includes the use of gas in hotels, clubs, restaurants, stores, business establishments, and the like. Industry uses gas for various heating operations, in manufacturing, heat treatment, atmosphere control, welding, etc. The chemical field where coal gas is used for the production of other materials is of recent development.

The first practical use of coal gas was made by William Murdock, a Scotch engineer, in the year 1792. He distilled coal in an iron retort and by the use of copper and tin pipes lighted his home with coal gas. Coal gas now offered the world a means of bringing light where darkness formerly existed. Later Murdock was employed by James Watt, the inventor of the steam engine, and lighted one of his foundries with the recently discovered coal gas. This new form of gas lighting attracted wide attention at a public exhibition in 1802 at the time of the signing of the Peace of Amiens.

The first gas company started in London in 1812 by a special charter granted by Parliament. It made gas by heating coal and lighted Westminster Bridge. The success of gas lighting in London resulted in its rapid spread to other countries. In the United States, Baltimore was the first city to light its streets with coal gas in 1816. Thus, the first use of gas was for street lighting. Later public buildings were lighted in this manner, and a few wealthy citizens also lighted their homes with coal gas. It was not until 1865 to 1875 that the use of gas for home lighting began to make any great progress.

The modern Bunsen burner was invented in 1855. This burner, premixing gas and air, made it possible to burn gas more economically with an intensely hot but smokeless flame. It was this development that was instrumental in giving a great impetus to the further use of gas.

Bituminous coals known as gas coals when heated to a high temperature out of contact with air yield coal gas. A variety of coal gases with different compositions and heating value are produced, depending upon the equipment, temperatures, and the process of manufacture. Typical analyses of purified coal gases are presented in Table I.

TABLE I

TYPICAL GAS ANALYSES

(Constituents in Percent by Volume)

| | Coal Gas | | | |
	Horizontal Retort	Inclined Retort	Continuous Vertical Retort	Coke-Oven Gas
Carbon dioxide	2.4	1.7	3.0	2.0
Oxygen	0.8	0.8	0.2	0.3
Nitrogen	11.3	8.1	4.4	4.8
Carbon monoxide	7.4	7.3	10.9	5.5
Hydrogen	48.0	49.5	54.5	51.9
Methane	27.1	29.2	24.2	32.3
Illuminants	3.0	3.4	2.8	3.2
Specific gravity	0.47	0.47	0.42	0.40
Btu per cubic foot (60° F, 30 inches of mercury, dry)				
Gross	542	599	532	569
Net	486	540	477	509

Examination of Table I shows that coal gases consist mainly of hydrogen, around 50 percent; methane, 24 to 32 percent; carbon monoxide, 6 to 13 percent; nitrogen, 4 to 11 percent; and smaller quantities of illuminants, carbon dioxide, and oxygen. The types of coal gases shown differ but little from one another in general characteristics.

Coke-oven gas is produced in an analogous manner to retort coal gas, but the size of the charge, operating temperatures, and other features of the process are different. A complete analysis of coke-oven gas is presented in Table II, where the gases included under the term "illuminants" have been separated by special low-temperature fractional analysis. The principal gases usually included under illuminants are ethylene, propylene, butylene, benzene, toluene, xylene, and acetylene.

COMBUSTION

The chemical union of oxygen with other elements has been termed oxidation. When union of oxygen with a combustible substance occurs, the process is known as com-

TABLE II

ANALYSIS OF COKE-OVEN GAS [1]

Gas from Koppers Ovens

Component	Unwashed	Washed with Straw Oil and Light Oil Removed
Hydrogen sulfide	0.7	0.7
Carbon dioxide	1.7	1.5
Nitrogen	0.9	1.0
Hydrogen	56.7	57.2
Carbon monoxide	5.7	5.8
Methane	29.6	29.2
Ethane	1.28	1.35
Illuminants:		
Ethylene	2.45	2.50
Propane	0.08	0.11
Propylene	0.31	0.29
Butane	0.02	0.04
Butylene	0.16	0.18
Acetylene	0.05	0.05
Light-oil fraction	0.65	0.13

bustion. The combustion or burning of materials is accompanied by the evolution of light and the rapid liberation of heat. Coal gas on burning unites with oxygen, producing light and liberating heat. For a full understanding of how this process occurs, and for the proper application and use of coal gas, the chemistry of combustion must be considered briefly.

Fuels are generally classified into three classes, namely, solid, liquid, and gaseous. The solid fuels include coal, lignite, wood, peat, charcoal, and coke. The liquid fuels comprise liquid petroleum products, alcohols, and tar and oils from coal carbonization. The more important gaseous fuels include coal gas, water gas, producer gas, refinery gas, and natural gas.

[1] American Gas Association, *Fuel-Flue Gases*, Am. Gas Assoc., New York, 1940, 198 pp.

For all practical purposes *combustion of fuels consists of* the chemical union of carbon, hydrogen, sulfur, or their compounds with oxygen. Combustion calculations and their application to utilization problems are based on a few simple laws as follows:

1. *Law of the conservation of matter,* which states that matter cannot be created or destroyed.

2. *Law of the conservation of energy,* which states that energy cannot be created or destroyed.

3. *Law of combining weights,* often called the law of reciprocal proportions, which states that the weights of elements or compounds which combine with each other have a definite simple relationship.

4. *The gas law,* which states that the volume of a gas is directly proportional to its absolute temperature and inversely proportional to its absolute pressure.

The number of chemical reactions involved in combustion processes are few, and those of prime importance are presented in Table III.

To simplify combustion calculations, the pound mole system is used. "Pound mole" is merely an abbreviation of the pound-molecular weight, which represents the molecular weight in pounds of the given substance, in place of the molecular weight in grams so common in scientific investigations. The equations in Table III show the heat evolved or absorbed on the basis of a pound mole of the reacting material. Equation 2 indicates that 1 pound mole of carbon (12 pounds), when burned to carbon dioxide, liberates 174,530 Btu. Equations 3 and 4 show the heat to be supplied to cause the reaction to take place.

COMBUSTION CALCULATIONS

The field of gas utilization involves many items of interest and value which can be directly calculated or derived from the gas analysis. The steps in the calculation of combustion data are illustrated by the application to a specific gas, but the principles involved are the same for other gases. For convenience, reference is made to Table

TABLE III

CHEMICAL REACTIONS

	Combustible Substance	Reaction	Btu per Pound Mole
(1)	Carbon to carbon monoxide	$C + \frac{1}{2}O_2 = CO$	+ 54,000
(2)	Carbon to carbon dioxide	$C + O_2 = CO_2$	+ 174,000
(3)	Carbon + carbon dioxide	$C + CO_2 = 2CO$	− 70,200
(4)	Carbon + water vapor	$C + H_2O = CO + H_2$	− 71,000
(5)	Carbon + water	$C + 2H_2O = CO_2 + 2H_2$	− 72,000
(6)	Carbon monoxide	$CO + \frac{1}{2}O_2 = CO_2$	+ 122,400
(7)	Carbon monoxide + water	$CO + H_2O = CO_2 + H_2$	− 700
(8)	Hydrogen	$H_2 + \frac{1}{2}O_2 = H_2O$	+ 123,100
(9)	Sulfur to sulfur dioxide	$S + O_2 = SO_2$	+ 126,000
(10)	Sulfur to sulfur trioxide	$S + \frac{3}{2}O_2 = SO_3$	+ 20,500
(11)	Methane	$CH_4 + 2O_2 = CO_2 + 2H_2O$	+ 382,000
(12)	Ethane	$C_2H_6 + \frac{7}{2}O_2 = 2CO_2 + 3H_2O$	+ 667,000
(13)	Propane	$C_3H_8 + 5O_2 = 3CO_2 + 4H_2O$	+ 950,000
(14)	Butane	$C_4H_{10} + \frac{13}{2}O_2 = 4CO_2 + 5H_2O$	+ 1,232,000
(15)	Acetylene	$C_2H_2 + \frac{5}{2}O_2 = 2CO_2 + H_2O$	+ 550,000
(16)	Ethylene	$C_2H_4 + 3O_2 = 2CO_2 + 2H_2O$	+ 600,000
(17)	Benzene	$C_6H_6 + \frac{15}{2}O_2 = 6CO_2 + 3H_2O$	+ 1,360,000

IV, in which the physical constants and combustion data are given for all the common chemical compounds which may be a part of the mixture. The first step is to set up a combustion table and chart. What follows is adapted from *Fuel-Flue Gases*.[1]

First write down the analysis of 1 cubic foot of the gas in a vertical column at the left-hand side of a large sheet of paper as shown in Table V. Note that the illuminants, in this case ethane and benzene, are shown divided. In column 2, the amount of oxygen required is entered. Since the gas contains some oxygen which will help in combustion, this appears as a negative quantity in the second column. The other amounts of oxygen result from multiplying the values in column 1 by the number of cubic feet of oxygen required for combustion per cubic foot of combustible as given in Table IV. This column adds up to 0.9895 cubic foot, and this sum is divided by the percentage of oxygen in air (20.99). The quotient 4.714 is shown in the third column and, underneath it, the amount of water vapor which would be carried by the air and the gas.

In the case of the gas, if saturated at 60° F, the amount of water vapor would be 0.0174 cubic foot, and if the air were 40 percent saturated at the same temperature, there would be

$$4.714 \times 0.40 \times 0.0174 = 0.034 \text{ cubic foot}$$

The sum of the moisture in the gas and air, 0.051, appears in the third column in the appropriate place.

The first conclusion to be drawn from these results is that for perfect combustion this gas would require 4.714 cubic feet of air for each cubic foot of dry gas burned. This corresponds to 1.0174 cubic feet of metered gas. This figure will be useful in calculating the excess air.

The next four columns deal with the calculation of the products of perfect combustion. The values result from multiplying the appropriate data in Table IV by the composition of this gas, as in the first column. Of course, the water vapor originally present is entered, and so are the amounts of carbon dioxide and nitrogen, including both the nitrogen in the gas and that which comes in with the combustion air. All the items are totaled both vertically and horizontally, and the figure 5.502 cubic feet is secured as the total volume of the products of combustion after they have been cooled to 60°. However, this is a theoretical figure because most of the water would have condensed under such conditions. The flue gases, however, would still be saturated with water vapor at 60°; consequently, to find the saturated volume, it is first necessary to deduct the amount of water vapor condensed and to add 1.74 percent to the dry volume to bring it to saturated conditions. This small percentage of added water behaves as a perfect gas. The amount equals

$$\underset{\substack{\text{Dry} \\ \text{volume}}}{4.466} + (\underset{\substack{\text{Volume} \\ \text{water vapor}}}{0.0174 \times 4.466}) = \underset{\substack{\text{Saturated} \\ \text{volume}}}{4.544} \text{ cubic feet}$$

Ultimate Carbon Dioxide. The ultimate carbon dioxide is the maximum percentage of carbon dioxide which can be found in the flue gases under perfect combustion conditions. It is useful as an index of the operating efficiency of the appliance. It is calculated as the quotient of the volume of carbon dioxide produced divided by the total dry volume. For this gas it would be

$$\frac{0.621}{4.466} \times 100 = 13.9 \text{ percent}$$

Either equation 1 or 2 may be used to calculate the ultimate carbon dioxide, as follows (see p. 1259):

TABLE

COMBUSTION

No.	Substance	Molecular Weight [*]	Pounds per Cubic Foot [†]	Cubic Feet per Pound [†]	Specific Gravity Air = 1.000 [†]	Heat of Combustion [‡]			
						Btu per Cubic Foot		Btu per Pound	
						Gross	Net [2]	Gross	Net [2]
1	Carbon	12.01	....	....	....	....	......	14,093 [4]	14,093 [4]
2	Hydrogen	2.016	0.005327	187.723	0.06959	325.0	275.0	61,100	51,623
3	Oxygen	32.000	0.08461	11.819	1.1053	......	......	......	......
4	Nitrogen (atmos.)	28.016	0.07439 §	13.443 §	0.9718 §	....	....	......	......
5	Carbon monoxide	28.01	0.07404	13.506	0.9672	321.8	321.8	4,347	4,347
6	Carbon dioxide	44.01	0.1170	8.548	1.5282	....	....	......	......
	Paraffin series C_nH_{2n+2}								
7	Methane	16.041	0.04243	23.565	0.5543	1,013.2	913.1	23,879	21,520
8	Ethane	30.067	0.08029 §	12.455 §	1.04882 §	1,792	1,641	22,320	20,432
9	Propane	44.092	0.1196 §	8.365 §	1.5617 §	2,590	2,385	21,661	19,944
10	n-Butane	58.118	0.1582 §	6.321 §	2.06654 §	3,370	3,113	21,308	19,680
11	Isobutane	58.118	0.1582 §	6.321 §	2.06654 §	3,363	3,105	21,257	19,629
12	n-Pentane	72.144	0.1904 §	5.252 §	2.4872 §	4,016	3,709	21,091	19,517
13	Isopentane	72.144	0.1904 §	5.252 §	2.4872 §	4,008	3,716	21,052	19,478
14	Neopentane	72.144	0.1904 §	5.252 §	2.4872 §	3,993	3,693	20,970	19,396
15	n-Hexane	86.169	0.2274 §	4.398 §	2.9704 §	4,762	4,412	20,940	19,403
	Olefin series C_nH_{2n}								
16	Ethylene	28.051	0.07456	13.412	0.9740	1,613.8	1,513.2	21,644	20,295
17	Propylene	42.077	0.1110 §	9.007 §	1.4504 §	2,336	2,186	21,041	19,691
18	n-Butene (Butylene)	56.102	0.1480 §	6.756 §	1.9336 §	3,084	2,885	20,840	19,496
19	Isobutene	56.102	0.1480 §	6.756 §	1.9336 §	3,068	2,869	20,730	19,382
20	n-Pentene	70.128	0.1852 §	5.400 §	2.4190 §	3,836	3,586	20,712	19,363
	Aromatic series C_nH_{2n-6}								
21	Benzene	78.107	0.2060 §	4.852 §	2.6920 §	3,751	3,601	18,210	17,480
22	Toluene	92.132	0.2431 §	4.113 §	3.1760 §	4,484	4,284	18,440	17,620
23	Xylene	106.158	0.2803 §	3.567 §	3.6618 §	5,230	4,980	18,650	17,760
	Miscellaneous gases								
24	Acetylene	26.036	0.06971	14.344	0.9107	1,499	1,448	21,500	20,776
25	Naphthalene	128.162	0.3384 §	2.955 §	4.4208 §	5,854 [3]	5,654 [3]	17,298 [3]	16,708 [3]
26	Methyl alcohol	32.041	0.0846 §	11.820 §	1.1052 §	867.9	768.0	10,259	9,078
27	Ethyl alcohol	46.067	0.1216 §	8.221 §	1.5890 §	1,600.3	1,450.5	13,161	11,929
28	Ammonia	17.031	0.0456 §	21.914 §	0.5961 §	441.1	365.1	9,668	8,001
29	Sulfur	32.06	.... ..	.. ..	....	....	... ..	3,983	3,983
30	Hydrogen sulfide	34.076	0.09109 §	10.979 §	1.1898 §	647	596	7,100	6,545
31	Sulfur dioxide	64.06	0.1733	5.770	2.264	....	....	... .	......
32	Water vapor	18.016	0.04758 §	21.017 §	0.6215 §	....	. ....	... .	......
33	Air	28.9	0.07655	13.063	1.0000	..... .	....	... .	... ..

All gas volumes corrected to 60° F and 30 in. Hg, dry. For gases saturated with water at 60° F, 1.74 percent of the Btu value must be deducted.

* Calculated from atomic weights given in *J. Am. Chem. Soc.,* **59**, 225 (1937).

† Densities calculated from values given in grams per liter at 0° C and 760 mm in the *International Critical Tables,* allowing for the known deviations from the gas laws. Where the coefficient of expansion was not available, the assumed value was taken as 0.0037 per °C. Compare this with 0.003662, which is the coefficient for a perfect gas. Where no densities were available the volume of the mole was taken as 22.4115 liters.

‡ Converted to mean Btu per pound (1/180 of the heat per pound of water from 32° F to 212° F) **from data by F. D. Rossini,** National Bureau of Standards, letter of April 10, 1937, except as noted.

IV

CONSTANTS [1]

| Cubic Feet per Cubic Foot of Combustible | | | | | | Pounds per Pound of Combustible | | | | | | Experimental Error in Heat of Combustion Percent + or - |
| Required for Combustion | | | Flue Products | | | Required for Combustion | | | Flue Products | | | |
Oxygen	Nitrogen	Air	Carbon Dioxide	Water	Nitrogen	Oxygen	Nitrogen	Air	Carbon Dioxide	Hydrogen	Nitrogen	
...	.....	.....	...	...	.....	2.664	8.863	11.527	3.664	.....	8.863	0.012
0.5	1.882	2.382	...	1.0	1.882	7.937	26.407	34.344	.....	8.937	26.407	0.015
...	.....	.....	...	...	.....	....	.....	.. .	.....	.....	.. ...	.....
0.5	1.882	2.382	1.0	..	1.882	0.571	1.900	2.471	1.571	.....	1.900	0.045
...	.. ..	.....	...	..	.....	.....	......	. ...	.....	. ...	... ..	..
2.0	7.528	9.528	1.0	2.0	7.528	3.990	13.275	17.265	2.744	2.246	13.275	0.033
3.5	13.175	16.675	2.0	3.0	13.175	3.725	12.394	16.119	2.927	1.798	12.394	0.030
5.0	18.821	23.821	3.0	4.0	18.821	3.629	12.074	15.703	2.994	1.634	12.074	0.023
6 5	24.467	30 967	4 0	5 0	24 467	3.579	11 908	15 487	3.029	1.550	11 908	0.022
6.5	24.467	30.967	4.0	5.0	24.467	3.579	11.908	15.487	3.029	1.550	11.908	0.019
8.0	30.114	38.114	5.0	6.0	30.114	3.548	11.805	15.353	3.050	1.498	11.805	0.025
8.0	30.114	38.114	5.0	6.0	30.114	3.548	11.805	15.353	3.050	1.498	11.805	0.071
8.0	30.114	38.114	5.0	6.0	30.114	3.548	11.805	15.353	3.050	1.498	11.805	0.11
9.5	35.760	45.260	6.0	7.0	35.760	3.528	11.738	15.266	3.064	1.464	11.738	0.05
3.0	11.293	14.293	2.0	2.0	11.293	3.422	11.385	14.807	3.138	1.285	11.385	0.021
4.5	16.939	21.439	3.0	3.0	16.939	3.422	11.385	14.807	3.138	1.285	11.385	0.031
6.0	22.585	28.585	4.0	4.0	22.585	3.422	11.385	14.807	3.138	1.285	11.385	0.031
6.0	22.585	28.585	4.0	4.0	22.585	3.422	11.385	14.807	3.138	1.285	11.385	0.031
7.5	28.232	35.732	5.0	5.0	28.232	3.422	11.385	14.807	3.138	1.285	11.385	0.037
7.5	28.232	35.732	6.0	3.0	28.232	3.073	10.224	13.297	3.381	0.692	10.224	0.12
9.0	33.878	42.878	7.0	4.0	33.878	3.126	10.401	13.527	3.344	0.782	10.401	0.21
10.5	39.524	50.024	8.0	5.0	39.524	3.165	10.530	13.695	3.317	0.849	10.530	0.36
2.5	9.411	11.911	2.0	1.0	9.411	3.073	10.224	13.297	3.381	0.692	10.224	0.16
12.0	45.170	57.170	10.0	4.0	45.170	2.996	9.968	12.964	3.434	0.562	9.968	[3]
1.5	5.646	7.146	1.0	2.0	5.646	1.498	4.984	6.482	1.374	1.125	4.984	0.027
3.0	11.293	14.293	2.0	3.0	11.293	2.084	6.934	9.018	1.922	1.170	6.934	0.030
0.75	2.823	3.573	..	1.5	3.323	1.409	4.688	6.097	.	1.587	5.511	0.088
.. .	. ..	.....	...	..	.....	0.998	3.287	4.285	1.998 (SO$_2$)	.....	3.287	0.071
1.5	5.646	7.146	1.0 (SO$_2$)	1.0	5.646	1.409	4.688	6.097	1.880 (SO$_2$)	0.529	4.688	0.30
...	.....	.....	...	...	. ...	.. ..	.....	....	.....	.....	.. .	....
...	.....	.....	...	...	.....	.. ..	.....	..	.....	....	. ..	....
...	.....	.....	...	...	.....	... .	.....	...	.....	.....	... .	....

§ Denotes that either the density or the coefficient of expansion has been assumed. Some of the materials cannot exist as gases at 60° F and 30 in. Hg pressure, in which case the values are theoretical ones given for ease of calculation of gas problems. Under the actual concentrations in which these materials are present their partial pressure is low enough to keep them as gases.

2 Osborne, N. S., Stimson, H. F., and Ginnings, D. C., *Mech. Eng.*, **57**, 162–3 (1935). Osborne, N. S., Stimson, H. F., and Fiock, E. F., *Natl. Bur. Standards U. S., Research Paper* **209** (1930), 70 pp.

3 American Gas Association, *Combustion*, Am. Gas Assoc., New York, 3rd ed., 1932, 208 pp.

4 Rossini, F. D., and Jessup, R. S., *Natl. Bur. Standards U. S., Research Paper* **1141** (1938), 23 pp.

TABLE V

COMBUSTION TABLE [1]

Mixed Coke-Oven and Carburetted Water Gas

	Mixture before Combustion			Cubic Feet of Products of Combustion				Gross Btu 60–30 Dry	Net Btu 60–30 Dry
	Cu Ft of Gas	O_2 Required	Air and H_2O	H_2O	CO_2	N_2	Total		
CO_2	0 034				0 034		0 034		
O_2	0 003	−0 0030							
N_2	0 120					0 120	0 120		
CO	0 174	0 0870			0 174		0 174	56 2	56 2
H_2	0 368	0 1840		0 368			0 368	119 2	100 7
CH_4	0 249	0 4980		0 498	0 249		0 747	253 1	228 0
C_2H_4	0 037	0 1110		0 074	0 074		0 148	60 3	56 6
C_6H_6	0 015	0 1125		0 045	0 090		0 135	56 1	53 8
Dry air			4 714			3 725	3 725		
H_2O(air and gas)			0 051	0 051			0 051		
	1 000	0 9895		1 036	0 621	3 845	5 502	544 9	495 3
							Less 1 036		
							Volume (dry) 4 466		

$$\text{Ultimate } CO_2 = \frac{0.621}{4\ 466} = 13\ 9\% \qquad\qquad \text{Flue gas volume (dry)} = \frac{0\ 621 \times 100}{\%\ CO_2\ (\text{analysis})}$$

Volume of excess air = volume of flue gases (dry) − flue gas volume (dry) for perfect combustion, i e 4 466 for this gas

	% CO_2 by Flue Gas Analysis					Item No
	13 9	12 0	11 0	10 0	9 0	
Volume excess air		0 709	1 179	1 744	2 434	2
Nitrogen		3 845	3 845	3 845	3 845	3
Total $N_2 + O_2$		4 554	5 024	5 589	6 279	4
Volume oxygen		0 149	0 247	0 366	0 511	7
Percent excess air		15 1	25 0	37 0	51 7	6
Flue gas analysis % by volume $\{$ CO_2	13 9	12 0	11 0	10 0	9 0	8
O_2	0 0	2 8	4 4	5 9	7 4	9
N_2	86 1	85 2	84 6	84 1	83 6	10
Total	100 0	100 0	100 0	100 0	100 0	
Cubic feet of products of combustion per cubic foot of gas burned $\{$ CO_2	0 621	0 621	0 621	0 621	0 621	11
$O_2 + N_2$	3 845	4 554	5 024	5 589	6 279	5
Total dry	4 466	5 175	5 645	6 210	6 900	1
H_2O	1 036	1 036	1 036	1 036	1 036	12
Total wet	5 502	6 211	6 681	7 246	7 936	13
Partial pressures in atmospheres $\{$ CO_2	0 113	0 100	0 093	0 086	0 078	14
H_2O	0 188	0 167	0 155	0 143	0 130	15

Temp, °F	CO_2	H_2O	CO_2	H_2O	CO_2	H_2O	CO_2	H_2O	CO_2	H_2O
3,800	17 6	2 6								
3,700	14 4	2 1								
3 600	11 7	1 9	6 7	1 1	5 5		4 85		4 4	
3,500	9 5	1 6	4 8	0 8	4 0	0 7	3 50		3 2	
3 400	7 8	1 3	3 4	0 6	2 8	0 5	2 4		2 2	
3,200	4 2	0 8	1 5		1 2		1 05		0 95	
3,000	2 3	0 5	0 6		0 45		0 40		0 35	

(Percent dissociation of flue gases)

Flame temperature, °F	3,630	3,450	3 295	3 110	2,890

$$\text{Ultimate percent } CO_2 = \frac{\text{Cubic feet } CO_2 \text{ per cubic foot gas} \times 100}{\text{Total dry cubic feet flue gases}} \qquad (1)$$

or

$$\text{Ultimate percent } CO_2 = \frac{\text{Percent } CO_2 \text{ in flue-gas sample} \times 100}{100 - \dfrac{\text{Percent } O_2 \text{ in same sample}}{0.2099}} \qquad (2)$$

Volume of Flue Gases. Since the usual operating conditions for appliances require the use of excess air, this can be calculated in terms of the percentage of carbon dioxide. The total volume of flue gases rises with the excess air as the percentage of the carbon dioxide in the flue gas drops below the ultimate value. The following expression is used to calculate the volume of the flue gases.

$$\left.\begin{array}{l}\text{Total volume of}\\ \text{flue gases (dry)}\end{array}\right\} = \frac{\text{Cubic feet } CO_2 \text{ produced per cubic foot gas burned} \times 100}{\text{Percent } CO_2 \text{ by analysis}} \qquad (3)$$

Combustion tables are generally set up first for perfect combustion conditions and then for even whole-number percentages of carbon dioxide as is shown in the example which follows. This deals with the same gas that has already been used in the calculations.

Excess Air. Equation 4 shows the excess air in terms of the volume of dry flue gases as calculated from equation 3.

$$\left.\begin{array}{l}\text{Volume excess air} = \text{Volume flue gases}\\ \text{(dry) from eq. 3} - \text{Volume flue gas}\\ \text{(dry) for perfect combustion (4.544}\\ \text{for this gas)}\end{array}\right\} \; (4)$$

To use it for setting up a combustion table, it is customary to make a series of substitutions of the even-numbered percentages of carbon dioxide in equation 3, thus obtaining the dry-flue-gas volume corresponding to each even percent of dioxide, and this is included as shown at item 1 (the eleventh line of Table V). It is then necessary to subtract the dry-flue-gas volume for perfect combustion from each of these figures, and the resultant volume of excess

air is entered as item 2 at the head of Table V. Item 3 in the table is the cubic feet of nitrogen in the flue gases, which, in this example, is 3.845. The sum of items 2 and 3 gives the total nitrogen and oxygen in the flue gases. They are brought together in this way because the specific heat of these two gases is the same and later computations of the heat content of the flue gases will be facilitated. Item 5 is a repetition of item 4. Item 6 may now be calculated as a percentage of the volume of excess air. It is determined by dividing by the volume of air required for perfect combustion, in this case 4.714. Item 7 need be calculated only if dissociation calculations are going to be made later. It is, of course, 20.99 percent of the volume of excess air. Item 8 is the percentage of carbon dioxide in the flue-gas analysis. The first left-hand figure is the ultimate percentage of carbon dioxide, and the other values are even-numbered amounts arbitrarily selected for convenience. Item 9 is the percentage of oxygen in the flue gases determined by taking the ratio of item 7 to item 1. The percentage of nitrogen is determined by deducting the sum of items 8 and 9 from 100, yielding the values in item 10.

The next step is to determine the actual volume of the flue gases for varying percentages of carbon dioxide. This leads to writing down as item 11, directly over item 5, the volume of carbon dioxide produced per cubic foot of gas burned, which is 0.621 cubic foot in this example. This is a check

of the total dry volume by addition; the answer must be the value entered as item 1. In item 12, the amount of water vapor produced in the combustion of 1 cubic foot of gas is entered and the total wet flue gas volume obtained by adding items 1 and 12 to give the values for item 13. Then, if desired, items 14 and 15 showing the partial pressure of carbon dioxide and water in atmospheres may be entered. For carbon dioxide, the value is obtained by dividing item 11 by item 13; and for water, the result is obtained by dividing item 12 by item 13.

Heat-Content Chart. The method of drawing up a heat-content chart, up to temperatures of about 2,200° F, is a very simple matter because the dissociation effects need not be considered. For constructing a chart to cover the entire scale up to the flame temperature, reference should be made to the appropriate section in the *Fuel-Flue Gases.*[1]

Items 11, 5, and 12 are used to calculate the heat in the flue products. From a heat-content chart for carbon dioxide, water, and air, such as Fig. 1, or those given by Haslam and Russell,[5] similar data may be obtained on a molar basis. These charts give the heat content above 60° F of a unit volume of carbon dioxide, or water, or air for every temperature. By multiplying items 11, 5, and 12 by the values read from the chart and adding the results, the heat content of the particular gas in question is obtained. This is based on 60° F, which is convenient for most calculations.

The illustrative Tables V and VI show how the heat-content values used in plotting the chart of temperature versus heat content in the flue gases are obtained. This chart refers only to the sensible heat, and

5 Haslam, R. T., and Russell, R. P., *Fuels and Their Combustion*, McGraw-Hill Book Co., New York, 1926, 809 pp.

latent heat must still be considered. Before explaining the latent heat which is recovered from condensation of the water vapor to liquid water, it might be well to point out that a series of calculations as illustrated must be carried out for every value of carbon dioxide and for a large enough number of temperatures to permit plotting of smooth curves. To the values so obtained, it is necessary to add the latent heat.

In this case 1.036 cubic feet of water vapor is involved in combustion, and if it were to condense, heat would be liberated in the amount of 50.3 Btu for each cubic foot of water vapor. This unit figure is obtained by reference to the steam tables, and it has been worked out for convenience in calculating these charts.

$$50.3 \times 1.036 = 52.1 \text{ Btu}$$

This amount must be added to each of the totals given in Table VI. Thus the same values are obtained which can be read opposite the appropriate temperatures and carbon dioxide on the chart.

The dissociation of gases plays an important part in many applications of fuel gas, particularly at elevated temperatures. Likewise, the calculation of flame temperature which is a purely theoretical value has a number of special uses. For a complete discussion of these factors, reference should be made to *Fuel-Flue Gases.*[1]

The approximate volume of theoretical air required and the resulting flue products for different types of fuels are given in Table VII.

DEW POINT

Information relative to the dew points of flue gases is important owing to the improvement in design and control of gas equipment to obtain the maximum recovery of available heat. Normally, the dew point can be determined by calculating the
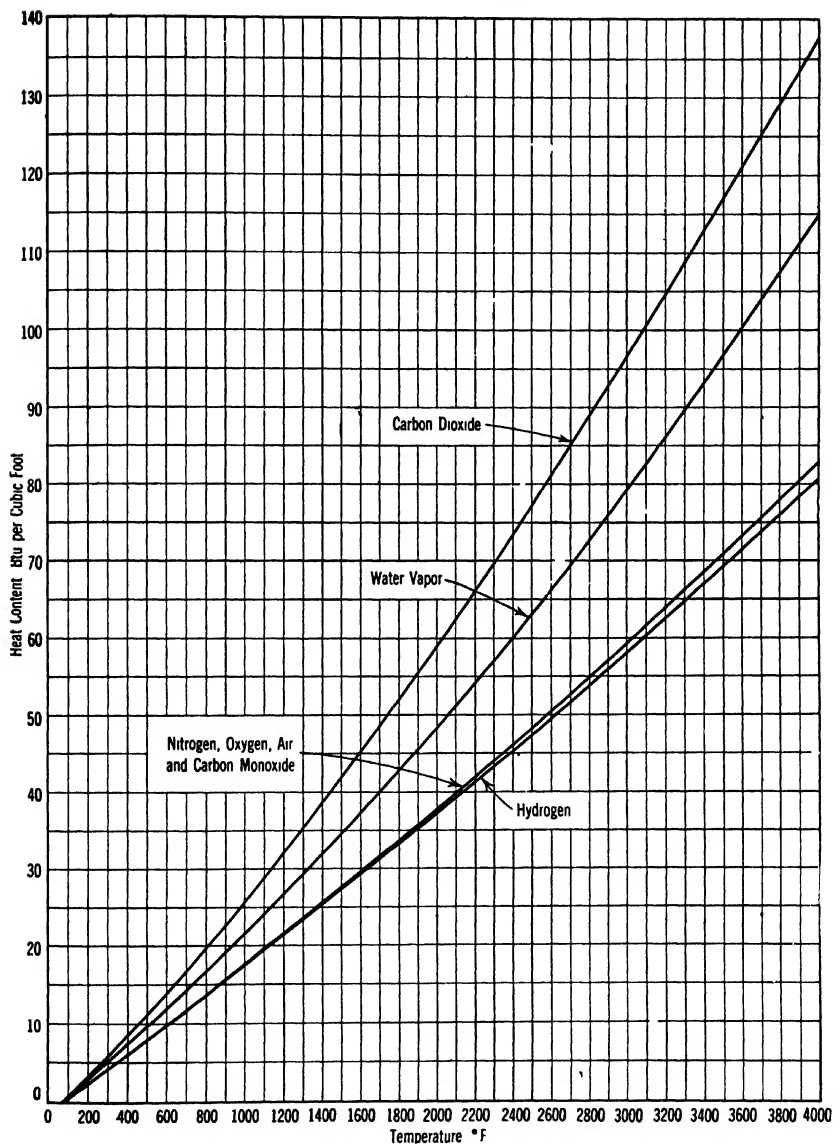
FIG. 1. Heat content, above 60° F, of gases found in flue products.[1]

TABLE VI

ILLUSTRATIVE CALCULATION OF HEAT CONTENT FOR CONSTRUCTING CHART

Heat in 1 Cubic Foot of:		Temperature, °F		
		1,000	1,200	1,800
Carbon dioxide		26 Btu	32 Btu	52 Btu
Water		22	27	42
Oxygen + nitrogen		18	22	34

		13.9 Percent Carbon Dioxide Heat Content of Fuel Gases at		
Volume of:		1,000° F	1,200° F	1,800° F
Carbon dioxide (item 11)	0.621 cu ft	16.1 Btu	19.8 Btu	32.3 Btu
Water (item 12)	1.036	22.8	28.0	43.5
Oxygen + nitrogen (item 5)	3.845	69.2	84.6	130.8
Total		108.1	132.4	206.6

		11 Percent Carbon Dioxide Heat Content of Flue Gases at		
Volume of:		1,000° F	1,200° F	1,800° F
Carbon dioxide (item 11)	0.621 cu ft	16.1 Btu	19.8 Btu	32.3 Btu
Water (item 12)	1.036	22.8	28.0	43.5
Oxygen + nitrogen (item 5)	5.024	90.5	110.7	171.0
Total		129.4	158.5	246.8

TABLE VII

ESTIMATION OF APPROXIMATE VOLUME OF THEORETICAL AIR REQUIRED AND VOLUME OF RESULTING FLUE PRODUCTS

	Cubic Feet per Pound of Solid Fuels	Approximate Accuracy, percent	Exceptions
Theoretical air required	Btu per pound × 0.0097	3	Fuels containing more than
Total flue products	Btu per pound × 0.0106	3	30 percent water
Total water in flue products	Btu per pound × 0.0008	50	

	Cubic Feet per Pound of Liquid Fuels		
Theoretical air required	Btu per pound × 0.0094	3	Results low for gasoline and
Total flue products	Btu per pound × 0.0099	3	kerosene
Total water in flue products	Btu per pound × 0.0010	20	

	Cubic Feet per Cubic Foot of Gaseous Fuels		
Theoretical air required	Btu per cubic foot × 0.0089	5	Gases of 300 Btu per cubic
Total flue products	Btu per cubic foot × 0.0104	5	foot or less
Total water in flue products	Btu per cubic foot × 0.0020	10	

amount of water vapor present in the flue gas in any combustion condition as outlined in the previous section. From the percentage of water vapor obtained, the dew point can be readily determined by reference to appropriate humidity charts. However, the dew points of the flue products resulting from the combustion of sulfur-bearing industrial fuels with varying

FIG. 2. Dew points of industrial gases as a function of $\dfrac{\text{grains sulfur per 100 cubic feet}}{\text{Btu per cubic foot}}$.

amounts of excess air are different from those calculated from the water vapor alone.

The dew point for industrial fuel gases can be estimated by reference to Fig. 2, which shows the probable effect of increasing the sulfur content upon the dew point of the flue products with increasing amounts of excess air.[6]

For example, a manufactured gas with a calorific value of 550 Btu per cubic foot and containing 15 grains of sulfur per 100 cubic feet is burned with 40 percent excess

6 Yeaw, J. S., and Shnidman, L., *Ind. Eng. Chem.*, **27**, 1476–9 (1935), **28**, 999–1004 (1936); *Power Plant Eng.*, **48**, No. 1, 68–71, No. 2, 69–71, No. 3, 73–5 (1943); unpublished data. See also p. 180 of ref. 1.

air. The proper curve on Fig. 2 is chosen as shown by

$$\frac{\text{Grams sulfur per 100 cubic feet}}{\text{Btu per cubic foot}} \times 100$$

or

$$\frac{15}{550} \times 100 = 2.7$$

This represents an imaginary curve lying between that shown for 0 and that for 3, and it is close to the 3 curve. This imaginary curve represents the true dew point of all the flue-gas mixtures containing any amount of excess air. For a mixture with 40 percent excess air, the true dew point is about 160° F.

MECHANISM OF COMBUSTION

Since the combustibles in coal gas consist essentially of hydrogen, carbon monoxide, and hydrocarbons, a consideration of these gases will be required to understand the phenomena of combustion. Different theories have been proposed by various investigators from time to time. However, the modern theory of the mechanism of combustion appears to be based on the researches of Bone and his collaborators,[7] Hinshelwood and Williamson,[8] Semenoff and his collaborators,[9] and Lewis and von Elbe.[10] These authors have described rather completely and theoretically the various fields advanced in the chemical reac-

7 Bone, W. A., and Townend, D. T. A., *Flame and Combustion in Gases*, Longmans, Green & Co., London, 1927, 548 pp. Bone, W. A., Newitt, D. M., and Townend, D. T. A., *Gaseous Combustion at High Pressures*, Longmans, Green & Co., London, 1929, 396 pp.

8 Hinshelwood, C. N., and Williamson, A. T., *The Reaction between Hydrogen and Oxygen*, Oxford University Press, Oxford, 1934, 108 pp.

9 Kopp, D., Kovalskii, A., Sagulin, A., and Semenoff, N., *Z. physik. Chem.*, **B6**, 307–29 (1930).

10 Lewis, B., and von Elbe, G., *Combustion, Flames, and Explosions of Gases*, Cambridge University Press, London, 1938, 415 pp.

tions responsible for the phenomena of combustion and flames.[11]

Since the combustion of hydrogen and carbon monoxide differs from that of gaseous hydrocarbons, each must be considered separately. When hydrocarbons burn in contact with air or oxygen, there is first an induction period during which an addition or association of the hydrocarbon molecule with oxygen occurs, forming unstable hydroxylated compounds which further react to form aldehydes. The aldehydes thus produced are further oxidized until formaldehyde results. The formaldehyde may break down thermally to produce carbon monoxide and hydrogen, or it may burn to form either carbon monoxide and water or carbon dioxide and water, depending upon the amount of oxygen present and available. This phenomenon of hydroxylation is a rapid process under suitable conditions. In mixtures of methane and hydrogen or methane and carbon monoxide, it has been found that the hydrocarbon, i.e., the methane, burns more rapidly than either the hydrogen or carbon monoxide. If enough oxygen is present to transform all the hydrocarbons to formaldehyde, combustion will take place without the formation of soot. What has been said applies to the lower members in the hydrocarbon series. The higher and more complex hydrocarbons, on the other hand, tend to decom-

pose into carbon and hydrogen by cracking, especially at the high temperature involved.

In the combustion taking place in the flame of an ordinary atmospheric burner, there is an equilibrium between the hydroxylation and the combustion of the hydrocarbons. Depending upon the proper air adjustment, a clean burning or a smoky flame will result. An excess of oxygen, lower temperature, and a proper mixing aid in the formation of hydroxylated compounds. The absence of these conditions gives rise to decomposition and a smoky flame. Particularly since 1930, some investigators have described and explained the combustion reaction as a chain reaction which when once initiated proceeds rapidly and completely to its finish. The chain-reaction theory is very useful in understanding much of the unusual behavior in the combustion of hydrocarbons. Since hydrocarbons may first react to form carbon monoxide and hydrogen, the combustion of hydrocarbons may be regarded as similar to the combustion of hydrogen and carbon monoxide.

The fundamentals of chain reactions have likewise been found useful in describing the exact mechanism of the combustion of carbon monoxide and hydrogen. The conditions that one would encounter in a flame of an ordinary atmospheric burner would be quiet burning under approximately atmospheric pressure, a temperature range of 1,000 to 2,500° F with combustion occurring at free uncatalyzed surfaces in the presence of an excess of oxygen. When both hydrogen and carbon monoxide are present, hydrogen burns approximately three times as rapidly as the carbon monoxide. Since, as indicated above, hydrocarbons, depending upon the conditions of combustion, may first react to form carbon monoxide and hydrogen, the phenomena of

11 Lewis, B., *Chem. Revs.*, **21**, 209–11 (1937). Brewer, A. K., *ibid.*, **21**, 213–9 (1937). Bradford, B. W., and Finch, G. I., *ibid.*, **21**, 221–44 (1937). Landau, H. G., *ibid.*, **21**, 245–57 (1937). Townend, D. T. A., *ibid.*, **21**, 259–78 (1937). Pease, R. N., *ibid.*, **21**, 279–86 (1937). Harris, E. J., and Egerton, A., *ibid.*, **21**, 287–97 (1937). Newitt, D. M., *ibid.*, **21**, 299–317 (1937). Von Elbe, G., and Lewis, B., *ibid.*, **21**, 319–28, 413–20 (1937). Kassel, L. S., *ibid.*, **21**, 331–45 (1937). Lewis, B., and von Elbe, G., *ibid.*, **21**, 347–58 (1937). Coward, H. F., and Payman, W., *ibid*, **21**, 359–66 (1937). Fiock, E. F., and Marvin, C. F., Jr., *ibid.*, **21**, 367–87 (1937). Smith, F. A., *ibid.*, **21**, 389–412 (1937). Jones, G. W., *ibid.*, **22**, 1–26 (1937).

combustion of these compounds are similar to those of hydrogen and carbon monoxide.

The simplest type of gas flame occurs when a gas such as coal gas is burned at the open end of a tube without previous mixture with air. As a result a luminous flame is produced, which has three cones: an innermost cone containing unburned gas, a visible luminous sheath where partial combustion with oxygen is taking place, and finally the nonluminous sheath where complete combustion occurs. In the luminous sheath the illuminants of the gas, i.e., ethylene and benzene, undergo thermal decomposition resulting in the formation of free carbon which on heating to incandescence gives rise to luminosity of the flame. This type of flame was formerly used to a large extent in gas lighting. At the present time it is used in special heating operations where the flame is brought in intermittent contact with material to be heated, especially when radiation is desired or where the deposition of free carbon on the object is desired.

The Bunsen burner shown in Fig. 3 represents the first real development in the design of gas burners, which permitted the wide and varied applications that are encountered today. A Bunsen burner differs from the open-jet burner described above in that it permits the premixture of gas with air, thereby resulting in a stable nonluminous flame; the gas supply is restricted by an orifice, the increased velocity inspirating primary air through the openings provided just beyond the orifice. This mixture of primary air and gas travels through the tube of the burner, which on combustion gives rise to a flame of three distinct cones: an inner cone, consisting of an unburned mixture of gas and air, a highly colored region where partial combustion or hydroxylation with air takes place, and

finally an outer mantle where secondary air enters, resulting in the complete combustion of the gas. A study of Fig. 3 showing the Bunsen burner and flame will make these considerations clearer. Complete discussions of gas-burner design can be found in recent publications.[12]

Diffusion of Secondary Air into this Zone Completes the Combustion Reactions. The Final Products are CO_2, H_2O, and N_2

Partial Combustion with Primary Air (Hydroxylation)

Unburned Mixture of Gas and Air.

Primary Air

Gas Orifice

Gas Supply
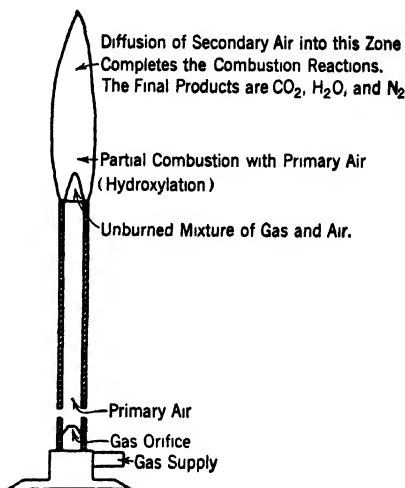
Fig. 3. The Bunsen burner.[3]

ATMOSPHERIC BURNERS

The majority of the atmospheric burners are of the Bunsen type, wherein primary air is inspirated with the gas to produce a flame of definite characteristics with a high heat intensity. These atmospheric burners are used almost entirely in residential appliances and for many industrial and commercial applications, and they account for the greater share of the business of the gas industry. The requirements of a satisfactory atmospheric burner include the following: (1) Combustion must be complete; neither carbon nor carbon monoxide must

12 Anon., *Am. Gas Assoc., Bull.* **10** (1940), 182 pp., *ibid.,* **13** (1942), 119 pp.

escape from the flame. (2) The flames must not lift or be blown from the ports. (3) The flame must not "back-fire" or "flash back." (4) The heat must be applied as efficiently as is consistent with good practice in other respects. (5) The flame must travel readily from port to port when the gas is lighted. (6) The distribution of heat with respect to its application must be satisfactory. Attention to this requirement

the manner in which the heat is to be applied.

2. Determine the arrangement of ports and provide for the escape of products of combustion with a view to insuring a uniform flow of secondary air to and away from each port with as little excess as is needed.

3. Determine the number and size of ports, making the number as large as can
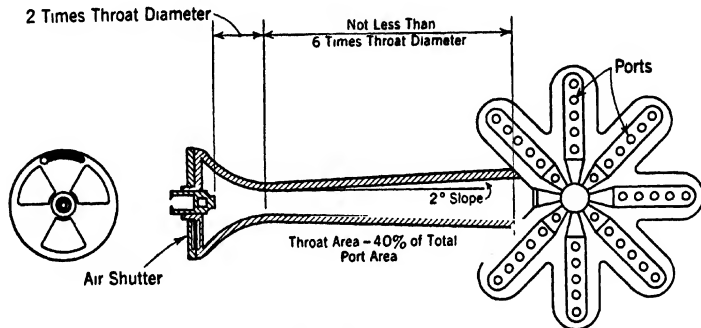
FIG. 4. Relative dimensions of a domestic gas burner to attain the maximum entrainment of primary air.[14]

is of importance in some appliances, but not in others. (7) Unusually difficult or expensive construction must not be involved unless it results in compensating advantages.

Figure 4 shows the relative dimensions of a residential atmospheric gas burner.[13] The proper design and adjustment of these burners to give satisfactory operation with a fuel gas of constant composition is a complex problem. The fundamentals involved in design have been summarized as follows:[14]

1. Determine the general shape and size of the burner from the space available and

be provided for without excessive cost, and choosing a size which will permit a maximum of primary air without danger of either back-firing or lifting.

4. Design the burner head of liberal size and with deep metal, through which the ports are machined.

5. Design the passages of the burner without abrupt changes in size or direction so that the stream of gas and air will expand gradually and approach the ports at low and uniform velocity.

6. Select tentatively, for each of as many sets of conditions as seem necessary to cover the range of conditions in which the appliance is to be used, an orifice of area a, using the formula

$$q = 1{,}300a \sqrt{\frac{h}{d}}$$

13 Eiseman, J. H., Weaver, E. R., and Smith, F. A., *Natl. Bur. Standards U. S., Research Paper* 446 (1932), 41 pp.

14 Anon., *Natl. Bur. Standards U. S., Circ.* 394 (1931), 25 pp.

where q is the maximum desirable volume of gas in cubic feet per hour, h is the maximum gas pressure in inches of water, and d is the specific gravity of the gas referred to air.

7. Assume the desired ratio of primary air to total air required for complete combustion from experience.

8. Assume a value for a burner constant k, from experience with a burner of the same general form (in the absence of any previous knowledge k may be tentatively assumed equal to $0.8/P$, where P is the total area of the ports), and compute whether the burner tentatively planned will entrain the desired amount of primary air under each set of conditions assumed as representative of those to be met. Use the formula

$$\frac{Q}{q} = k \sqrt{\frac{d}{aD}}$$

where Q is the volume of primary mixture which flows per unit time, q is the volume of gas which flows per unit time, D is the specific gravity, referred to air, of the primary mixture, and a and d have the meanings stated in paragraph 6.

9. Having completed a model burner, determine by trial whether its performance is satisfactory within the range of air shutter adjustment with respect to (1) completeness of combustion at the maximum rate of heat supply with the gas having the greatest requirement of "air for complete combustion," (2) back-firing with the most rapidly burning gas at minimum rate, and (3) lifting of the flames with the slowest-burning gas at maximum rate.

10. Determine by trial the maximum primary air that will allow an ample factor of safety against unstable flames, and while using this high primary air place the burner or regulate secondary air to give as high efficiency as may be obtained while providing an ample factor of safety against incomplete combustion.

11. Select the orifice to be used with a particular gas supply by the aid of the formula given in paragraph 6, or a corresponding one for the type of orifice used if the orifice is known to give a result different from that of the formula. Then employ the formula given in paragraph 8, and a value of the burner constant k determined by observation on the model under conditions as nearly as possible like those of service, and determine that the entrainment of primary air will be satisfactory within the range of adjustment of the air shutter. If the air required for complete combustion of the future supply of gas is not known, assume that 9 cubic feet of air will be needed per 1,000 Btu.

Figure 5 shows the regions in which flashback, lifting, and yellow tips occur, and the limit of safe operation of the atmospheric burner.[13] These particular curves are for a carburetted water gas of 570 Btu, but they indicate what would be expected of a typical coal gas.

In the design of atmospheric burners that portion of air which mixes with the gas primary to combustion is called primary air. Any additional air required to better the combustion is obtained from the atmosphere surrounding the flame and is termed secondary air. If the amount of primary air which mixes with the gas in a burner is increased, a point is reached above which the flames will either blow off the ports or flash back into the burner. Likewise, if the primary air is decreased, a limit is reached below which the tip of the inner cone assumes a yellow color. The yellow luminosity increases still further as the primary air is reduced, as a result of the formation of finely divided particles of solid carbon which burn less readily than the gas from which they are formed. As a
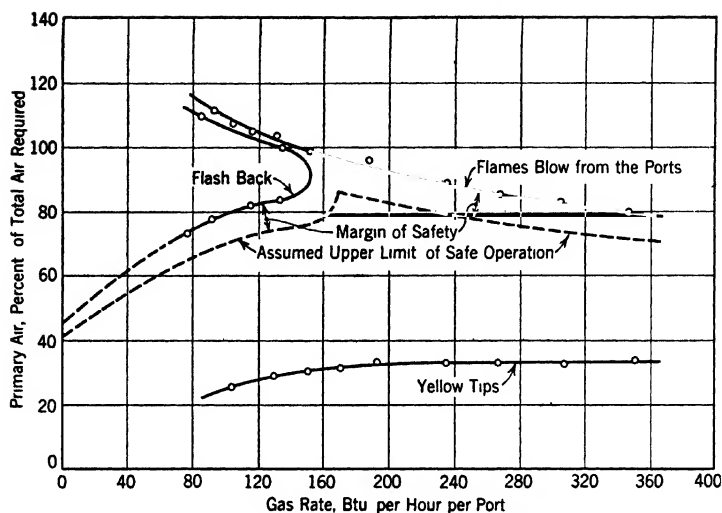
FIG 5. Boundaries of the regions in which flash-back, lifting, and yellow tips occur [18]
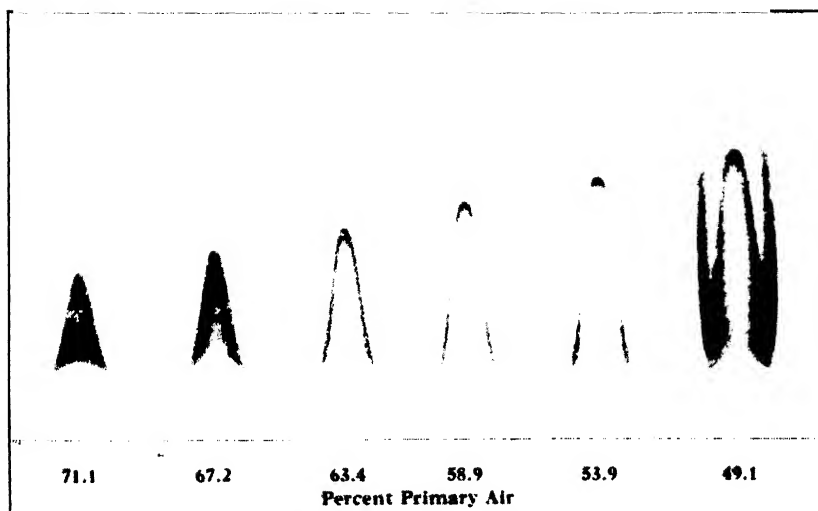
FIG. 6. Flames from coke-oven gas with different percentages of primary air.

rule the primary air inspiration of the atmospheric burner will be of the order of 50 percent of that theoretically required for complete combustion of the gas.

Figure 6 shows the combustion of a coke-oven gas with varying quantities of air, indicating how the flame becomes harder, has an important bearing on the burning characteristics of the gas.

Figure 7 shows the ignition velocity curves for various typical combustible gases with varying amounts of primary air. Study of flame-speed curves shows
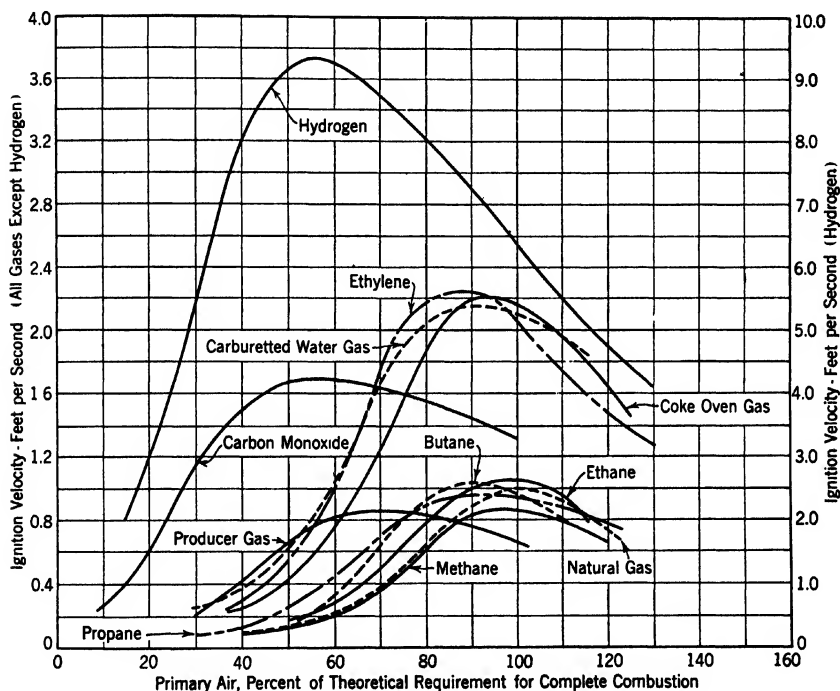
Fig. 7. Ignition velocity curves for various gases.[1]

dicating how the flame becomes harder, sharper, and smaller as the primary air is increased.

The combustion characteristics of coal gas when burned in an appliance in a typical burner are functions of its composition, its specific gravity, thermal value, and ignition characteristics. The rate of flame-speed travel or rate of flame propagation that the range of burner adjustment is greatest for gases having gradual slopes of the flame-speed curve. The flame velocity indicates to some extent the tendency for flash-back or blow-off. These generalizations are not intended to convey the impression that burner design is solely dependent upon flame speed. On investigation, it will be found that in all cases of

practical significance the mixture velocity through the ports is much greater than the rate of flame propagation, possibly several times as great. Apparently, the secondary combustion in the outer flame envelope is very important in its effect on stability of flames under certain conditions.

The ignition temperature of coal gas varies somewhat with the percentage of primary air but will be around 1,480° F. Again, the ignition temperature is a function of the composition, specific gravity, and percentage of primary air of the gas mixture. The maximum flame temperature possible from the coal gas is in the range of 3,500° F.

THE ADJUSTMENT OF FLAMES [15]

The proper and correct adjustment of flames in atmospheric burners is important not only for safety but also for efficiency of utilization. The characteristics of atmospheric burner flames are controlled by the primary air-gas ratio of the mixture in the burner head. If the calorific value of the burner-head mixture is reduced to about 100 Btu per cubic foot, most atmospheric burners will flash back. If the calorific value of the burner-head mixture is increased to about 250 Btu per cubic foot, the flames will be yellow tipped. Since both these conditions are to be avoided, and since both are readily identified, adjustments must be made within these limits.

In various references [16] in the literature it has been stated that the burner-head mixtures for atmospheric burners should be adjusted so that the calorific value of the

primary air-gas mixture is equal to 175 Btu per cubic foot in order to secure proper combustion characteristics for the flames. There is little evidence to support this contention or to show that such an adjustment is being made. In fact some evidence indicates that burners operate quite satisfactorily when set both above and below this adjustment.[12]

The characteristics of the Bunsen flame are controlled by the amount of primary air allowed to flow into the gas stream as it issues from the orifice and proceeds into the burner head. The flame produced consists of several parts. Inside the center of the flame there is an unburned mixture of gas and air moving forward at the same speed at which the flame is trying to move backward. This is noted particularly in flames 3, 4, and 5 of Fig. 8. The flame front is outlined by a brightly colored area often referred to as the inner cone. Its color is variously described as bright blue or green. A rapid chemical reaction involving a decomposition of the constituents of the fuel occurs in this area. It is sometimes called the hydroxylation area, as alcohols, aldehydes, carbon monoxide, and other partially oxidized constituents are formed there. The final and complete combustion takes place in the larger outer envelope which surrounds the inner cone. This part of the flame is usually only lightly colored, but it can be made more obvious by viewing against a black background or in a darkened room.

The proportion of air allowed to enter the burner head with the combustible gas determines the size and shape of the flame. As the amount of primary air is decreased, the flame front moves outward from the port, the inner cone becomes larger, and the brightly colored reaction zone surrounding it becomes thinner. This can be

[15] Shnidman, L., and Yeaw, J. S., *Gas Age-Record*, **88**, No. 8, 16–20, 32 (1941).

[16] Berry, W. M., Brumbaugh, I. V., Eiseman, J. H., Moulton, G. F., and Shawn, G. B., *Natl. Bur. Standards U. S., Tech. Paper* **222** (1922), 77 pp. Harper, R. B., *Proc. Am. Gas Assoc.*, **1931**, 813–45. Willien, L. J., *ibid.*, **1938**, 843–50.

noted in flames 1 to 5 of Fig. 8. As the fraction of air is further reduced, the color of the reaction zone slowly fades out, usually becoming fuzzy first at the tip of the inner cone, as can be noted by flames 5 to 7.

It will be apparent from this description that the general requirements for a Bunsen flame cover a range of primary air-gas adjustments which markedly affect the size, shape, and general characteristics of the

reaction zone, and the less distinct outer sheath in which the combustion is completed. Such flames are illustrated by flames 3, 4, and 5.

It has been shown that the heating efficiencies of open-flame burners adjusted with softer flames are higher than those for such burners adjusted for harder flames.[13] The heat distribution for enclosed burners has also been found to be better with softer rather than harder flame settings.
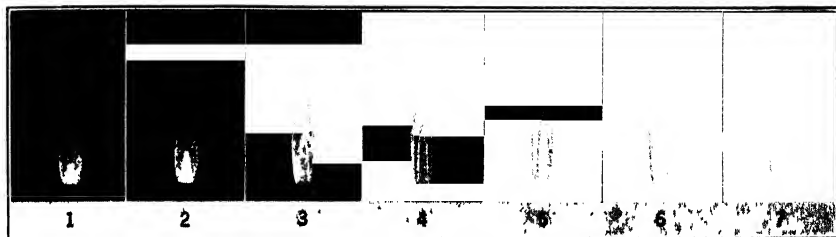
Fig. 8. Typical Bunsen burner flames with the percentage of primary air decreasing from left to right.

flame. Bunsen flames with high primary air are generally referred to as hard flames, for example, flames 1 and 2. They are characterized by short, sharply defined, and often fluttery flames, ignition and/or extinction noises, and general flash-back tendencies. Bunsen flames with low primary air are considered to be soft flames; they are characterized by longer, less sharply defined, and rather wavering flames, with a minimum of ignition or extinction noise or flash-back tendencies, for example, flames 6 and 7.

The characteristics of both hard flames and soft flames make them unsuitable for residential-appliance burners. Good Bunsen flames for residential-appliance burners should consist of three clearly defined parts: the relatively cool darkened inner zone, the brightly colored decomposition or

The correct type of flame should consist of the three previously prescribed, clearly defined sections. The primary air to the burner should be reduced until the brightly colored reaction zone has become as thin as possible and yet remains clearly defined without breaking or fuzziness. This may be taken as the definition of the characteristics of the proper flame which should be obtained on the burners. This type of flame is best illustrated by flame 5.

Other methods depending upon the analysis of air-gas mixtures in the burner head have been applied as a means of properly studying flames on burners. The procedures are expensive, cumbersome, and not suitable for the average gas service man. Therefore, the above-described, simple method has been found satisfactory for adjusting burners and is used commercially.

COMBUSTION CHARACTERISTICS OF FUEL GASES [17]

Until recently no attempt has been made to control the rate and manner of the combustion of a fuel gas, although this would seem to be most important. The reason for the omission may be the lack of a satisfactory definition of the combustion characteristics of a fuel gas, such as might correspond to the generally accepted calorific value. The physical and chemical properties of the gas before it is burned, as well as the corresponding properties of the resulting combustion products, enter into the problem, as do the type and design of the burner and the properties of the atmosphere in which the combustion takes place.

The burners most noticeably affected by changes in combustion characteristics of fuel gases are of the atmospheric or Bunsen type. It is not strange, therefore, that testing devices based upon the Bunsen type of burner have been designed to evaluate fuel gases. Generally speaking, these test burners consist of an atmospheric burner equipped with primary air or gas control devices which operate over an arbitrary scale, and the cone-forming properties of the flames are used to differentiate one gas from another. Such test burners are sensitive in their indications, and they reveal differences in the behavior of gases which would not otherwise have been discovered. The results are all expressed in independent and empirical units, and the test burners can be employed only after the scales have been calibrated in terms of the gas similar in character and composition to those that are to be checked. The range of usefulness of such a test instrument is therefore strictly limited. Among those which have

been developed and applied in practice are: [18]

Hofsäss burner in 1919 in Germany.
Grebel-Velter indicator in 1922 in France.
Ott burner in 1925 in Germany.
Gray calorimeter in 1934 in England.
Czakó and Schaack burner in 1934 in Germany.
Hawes burner in 1937 in England.
Aeration test burner in 1937 in England.

Besides the test burner numbers, there are a few gas quality index values which are calculated from the usual physical properties of the gas or from its analysis. These include: [18]

The Wobbe index in 1926 in Germany.
A.G.A. *C* factor [19] in 1933 in the United States.
Kennziffer in 1934 in Germany.
Flammenleistung in 1936 in Germany.
D function in 1937 in England.

No universally accepted test burner number or calculated index has yet been found which will meet all requirements. In Europe, considerable data have been obtained showing the relation between gas composition and test burner numbers, but there are very few corresponding appliance data. In the United States the American Gas Association has over 125,000 appliance tests on record but no corresponding test burner data. In neither locality can the results be applied without careful consideration of the several factors involved in any particular case.

In view of this state of affairs, it seems that one test burner would be about as satisfactory as another for all practical purposes. The principal differences appear to be in the mechanical refinements which

[17] Shnidman, L., and Yeaw, J. S., *Proc. Am. Gas Assoc.*, 1940, 682–713.

[18] Wood, J. W., and Eastwood, A. H., *40th Rept. Joint Research Com. Inst. Gas Engrs. and Leeds Univ. 1937*, 157 pp.; *Gas J.*, **220**, 464, 467–70, 649–52, 655–8 (1937); *Gas World*, **107**, 421–4 (1937).

[19] Anon., *Am. Gas Assoc. Testing Laboratory Rept.*, 089 (1938), 68 pp.

tend to enhance the accuracy of one as compared to another. Any Bunsen-type burner equipped with a suitable scale should serve to show differences between the combustion characteristics of various gas mixtures. Figure 9 shows the test burner used by the Rochester Gas and

FIG. 9. Rochester Gas and Electric Corporation's test burner.

Electric Corporation in measuring the characteristics of the gas. For a full and complete discussion of its use and application, reference should be made to the published article.[17]

Although literature [12, 13, 17, 20] is available which shows appropriate design data for burners consuming various fuel gases,

20 Berry, W. M., Brumbaugh, I. V., Moulton, G. F., and Shawn, G. B., *Natl. Bur. Standards U. S., Tech. Paper* **193** (1921), 62 pp. Mattocks, E. O., *Am. Gas Assoc. Monthly*, **16**, 188–93 (1934). Conner, R. M., *ibid.*, **16**, 41–5 (1934). Pacific Coast Gas Association, *Gas Engineers' Handbook*, McGraw-Hill Book Co., New York, 1934, pp. 921–36.

it is sometimes desirable to change the gas for which an appliance was adjusted. It is possible to determine by actual test the effect on appliance operation by changing from the adjustment gas to another gas. Indication of this effect may be predicted from the complete gas analyses of the two gases and by means of an empirical formula which is given later.

Changes or variations in gas supply may play a prominent part wherever gas is used. As readjustments of appliances are not desirable, it is essential that fuel characteristics be maintained within close limits. Appliances possess flexibility which permits reasonable variations in specific gravity and heating value. The range of changes in these properties is limited.

The air requirement to yield theoretically complete combustion is essential in designing a burner for a given gas. If the constituents of the gas are changed, about the same heating value and specific gravity being maintained, it is possible to change the air requirements. Unless the air adjustment of the burners is altered, incomplete combustion due to an insufficient amount of air, blow-off, or flash-back, caused by too much air, may occur.

Heating value is important in its effect on combustion. If an appliance is adjusted for a gas of a given heating value and this characteristic is increased beyond a certain limit, incomplete combustion may occur. A decrease in heating value may result in flash-back or lifting of flames.

The proper consumption of a given appliance or burner in Btu per hour is a constant, regardless of the heating value or other characteristics of the gas being served. If one gas is substituted for another of different heating value, the burner orifices should be adjusted so that the same number of Btu per hour will be burned as before. A Btu in one kind of gas is equal

in usefulness to a Btu in another kind of gas.

Specific gravity exerts its effect in two ways. Since the rate of gas flow through an orifice varies inversely as the square root of the specific gravity, it is apparent that any increase or decrease in this characteristic may result in either an insufficient or an excessive gas supply to an appliance. The second effect of specific gravity is on the quantity of primary air inspirated by an atmospheric burner.

If the fast-burning constituents of a gas, especially hydrogen, are increased, the rate of flame propagation of the gas will increase until flash-back and noisy extinction occur. On the other hand, if the slower-burning elements, like methane and ethane, are increased, the resulting rate of flame propagation will be slower. If all or most constituents of a fuel gas change, the problem of anticipating the effect on the rate of flame propagation becomes more complicated.

Research conducted by the American Gas Association Testing Laboratories on the utilization of various mixed fuel gases resulted in the establishment of certain limits in changes which may be made in controlling factors without resulting in unsatisfactory operation of the average appliance.[21] This work was conducted by adjusting several representative appliances using one gas and then without change in adjustment supplying the appliance with a second gas, the characteristics of which were different from those of the first.

When using manufactured gas from 500 to 600 Btu per cubic foot on typical domestic appliances, heating value of the gases should be maintained within plus or minus 5 percent and specific gravity might

[21] Anon., *Am. Gas Assoc. Testing Laboratory Rept.* **597** (1930), 61 pp., **645** (1932), 64 pp., **689** (1933), 68 pp.

be varied from 10 percent upward to 10 percent downward from the adjustment gas. More than 175,000 tests were conducted, and it was found possible to express an empirical relationship between two fuel gases. The equation developed is:

$$C = \frac{h_2 A_2 d_1}{h_1 A_1 d_2} + \frac{h_1 A_1}{5,000 E_1 F_1} - \frac{h_2 A_2}{5,000 E_2 F_2}$$

where C = index of change in performance of appliances. When the gas on which they have been adjusted to perform satisfactorily (adjustment gas) is to be replaced by another gas (test gas) the value of C should be held between 0.85 and 1.15.

h = gross or total heating value, Btu per cubic foot.

A = air theoretically required for complete combustion, cubic feet per cubic foot of gas.

d = specific gravity (air = 1.0).

E = the heat capacity of the theoretical products of combustion 60° F to 1,600° F, in Btu. $E = 0.029 V_{CO_2} + 0.023 V_{H_2O} + 0.0189 V_{N_2}$, where V is the volume of each product as indicated by the respective subscripts CO_2, H_2O, and N_2, formed by the combustion of 1 cubic foot of gas with the air theoretically required for complete combustion, in cubic feet, and 0.029, 0.023, and 0.0189 are the heat capacities of each product of combustion 60° F to 1,600° F, in Btu per cubic foot.

F = summation of the products of the mole fraction and a constant resolving each combustible constituent to the basis of equivalent free hydrogen. $F = H_2 + 5.36$ CO $+ 35.2$ illuminants,

$+ 27.3\ CH_4 + 38.7\ C_2H_6 + 80.8\ C_4H_{10}$, where H_2, CO, illuminants, etc., are the mole fractions of each combustible constituent in the gas.

1 and 2 = subscripts designating the adjustment gas and test gas, respectively.

The A.G.A. index C represents a quality index factor of the gas calculated from its physical properties. In order to obtain this factor, the gross heating value, specific gravity, and complete analysis must be available. The final results before adoption must be confirmed by limited experimental studies.

The advantage of the test burner, over any other method yet proposed as a measure of the combustion characteristics of a gas, lies in the fact that it is a direct test which corresponds closely to actual practical application. After the original calibration is completed, test results may be obtained quickly, easily, and directly. Furthermore, additional information concerning relative flame stabilities may also be obtained by simple readjustments of the air or gas supply to the test burner, and the effect upon relative cone heights and flash-back or blow-off tendencies may be studied.

LIMITS OF INFLAMMABILITY

Combustible gas or vapor when mixed in certain proportions with air may explode on being ignited. If small increments of combustible gas are successively mixed with air, a composition will be reached at which the mixture just becomes explosive. The concentration of combustible gas at this composition, referred to as "the lower explosive limit," represents the minimum concentration of the particular combustible gas or vapor in mixture with air that will propagate flame if ignited. If the concentration of combustible in this mixture is progressively increased, a composition will be reached at which the mixture again becomes nonexplosive. The concentration of combustible in the mixture just before this point is reached is known as "the upper explosive limit"; it represents the maximum concentration of the particular combustible gas or vapor in mixture with air that will propagate flame if ignited. Inert gases such as carbon dioxide and nitrogen narrow the explosive range. When these inert gases are mixed in suitable proportions with the combustible gas or vapor the formation of an explosive mixture can be prevented.

Confusion has arisen regarding the meaning of the terms "explosive limits," "inflammation limits," and "limits of inflammability." These different expressions, in the final analysis, mean the same thing. Some authorities regard explosive limits as those limiting mixtures within which flame will propagate through the entire volume of the mixture and develop pressure, whereas inflammation limits or limits of inflammability are regarded as those limiting mixtures within which flame will propagate through the mixture irrespective of whether or not pressure is developed.

The limits of inflammability of various combustible gases and vapors [22] are shown in Table VIII, and of mixtures of such gases [1] in Table IX.

From a knowledge of the limits of each combustible in air and the percentages of each combustible present in the mixture, the limits of inflammability of combustible mixtures can be calculated quite accurately for a great number of mixtures by the application of the so-called mixture

22 Coward, H. F., and Jones, G. W., *U. S. Bur. Mines, Bull.* **279** (1931), 114 pp.

TABLE VIII

Limits of Inflammability of Gases and Vapors [22]

Gas or Vapor	Limits in Air, percent				Limits in Oxygen, percent *			Oxygen Percentage below Which No Mixture Is Inflammable	
	Lower		Higher		Lower		Higher	Nitrogen as Diluent of Air	Carbon Dioxide as Diluent of Air
Hydrogen	4 1	*4 0*	74			*4 0*	94	5 0	5 9
Ammonia		*16*		*27*	*15*		*7)*		
Hydrogen sulfide		*4 3*		*45 5*					
Carbon disulfide	1 25		44	*50*					
Carbon monoxide	12 5		74					5 8	5 9
Methane	5 3	*(5 0)*	14	*15*		*> 4*	*5)*	12 1	14 6
Ethane	3 2		12 5			*4 1*	*60*	11 0	13 4
Propane	2 4		9 5					11 4	14 3
Butane	1 85		8 4					12 1	14 5
Isobutane	1 8		8 4						
Pentane	1 4		7 8					12 1	14 4
Isopentane		*1 3*							
Hexane	1 2		6 9					11 9	14 5
Heptane		*1 0*		*6 0*					
Octane	0 95								
Nonane		*0 8*							
Decane		*0 7*							
Ethylene	3 0	*2 75*	29		3 1	*2 9*	80	10 0	11 7
Propylene		*2 0*		*11 1*	2 1		53	11 5	14 1
Butylene		*1 7*		*9 0*					
Acetylene	2 5	*(2 3)*	80						
Benzene	1 4		6 7						
Toluene	1 4	*1 3*		*6 7*					
o-Xylene		*1 0*		*6 0*					
Cyclopropane		*2 4*		*10 3*		*2 45*	*63*		
Cyclohexane	1 3	*1 2*	8 3						
Methyl alcohol	7 3	*6 7*		*36 †*				*10 3*	*15 8*
Ethyl alcohol	4 3	*3 3*		*13 †*					
Ethyl ether	1 9	*1 85*	48			*2 1*	*82*		
Vinyl ether		*1 7*		*27*	1 8		5		
Acetaldehyde		*4 0*		*57*					
Croton aldehyde		*2 1*		*15 5 ‡*					
Hydrocyanic acid		*5 6*		*40*					
Acetone	3 0	*2 55*	11	*13*				*13 5*	*15 6*
Methyl ethyl ketone		*1 8*		*10*					
Methyl propyl ketone		*1 5*		*5 ‡*					
Methyl butyl ketone		*1 2*		*8 ‡*					
Methyl acetate		*3 1*		*15 ‡*					
Ethyl acetate	2 0	*2 2*	8 5	*11 ‡*					
Propyl acetate	2 0	*1 8*		*8 0 ‡*					
Isopropyl acetate		*1 5*		*7 8 ‡*					
Butyl acetate	1 7 §								
Methyl chloride	10 7	*8 0*	17 4	*19*		*8 0*	*66 0*		
Methyl bromide		*13 5*		*14 5*					•
Ethyl chloride	4 2	*4 0*	14 3	*14 8*					•
Ethyl bromide		*6 7*		*11 2*					
Ethylene dichloride	6 2			*15 9 ‡*					•
Dichloroethylene	9 7		12 8						••
Propylene dichloride		*3 4*		*14 5 ‡*					•••
Amyl chloride		*1 4*							
Vinyl chloride	4 0		22 0						

* Values in italics were obtained in closed apparatus   Values in parentheses are for turbulent mixtures   † At 60° C   ‡ At 100° C   § At 30° C.

TABLE IX

INFLAMMABLE LIMITS OF MIXTURES [1]

Mixture		CO₂	Ill.	O₂	CO	H₂	CH₄	C₂H₆	N₂	H₂O	Btu per Cubic Foot	Explosive Limits Percent Gas in Air			
												Determined		Calculated	
Natural gas			.				97	3	0.0	..	1,034	4.8	14.0	4.9	14.0
Coke-oven gas		1.9	3.9	0.4	6.3	54.4	31.5	. .	1.6	.	631	5.0	28.4	4.5	28.1
Manufactured mixed gas		2.5	3.2	0.5	10.5	47.0	25.8	.	10.5	.	540	5.6	31.7	5.4	31.6
Carburetted blue gas		4.6	7.3	0.3	36.0	37.0	9.6	.	5.2		509	6.4	37.7	6.0	36.6
Blue gas		6.2	0.0	0.3	39.2	49.0	2.3	.	3.0	..	310	6.9	69.5	6.1	65.4
Producer gas		6.2		0.0	27.3	12.4	0.7	.	53.4	..	136	20.7	73.7	19.0	70.5
Dry quencher gas	(1)	3.9		0.1	5.9	33.3	2.5	.	54.3	..	153	12.3	64.4	11.8	66.5
	(2)	4.7	.	0.2	12.5	24.7	1.3	.	56.6	..	134	15.1	68.9	14.9	70.1
	(3)	7.0	.	0.1	7.6	13.2	1.0	.	71.1		78	26.7	73.0	26.5	71.4
Manufactured mixed gas + 80% steam		0.6	0.7	0.1	2.1	9.3	5.2	.	2.0	80.0		33.0	50.0	33.0	55.0
Producer gas + 50% steam		3.0	0.0	0.0	13.8	7.3		.	25.9	50.0		40.0	73.0	39.0	73.0
Mine fire gases	(1)					25.3	25.2		49.5			9.2	33.5	9.2	34.5
	(2)					16.6	16.7		66.7			14.0	40.0	14.0	41.5
	(3)				9.5	9.3	10.3		70.9			19.0	47.5	20.5	48.3
	(4)	0.5			3.7	1.0	36.7	.	58.2	.		14.0	27.0	13.0	27.0
	(5)	6.8			4.0	2.1	13.8		73.4	.		31.0	42.0	30.5	43.5
Gases from explosives	(1)	18.0			11.3	9.0	9.7		52.0			21.0	47.5	21.5	49.5
	(2)	15.0			10.0	7.3	7.8		60.0	.		26.0	51.0	26.0	51.5
Automobile exhaust gas	(1)	6.3			12.1	6.3	2.4		73.0			36.5	65.0	36.5	66.0
	(2)	7.8			7.6	4.1	1.4		79.2	.		55.5	67.0	58.0	68.0
Blast-furnace gas	(1)	15.9			23.7	4.3	0.2		55.9			36.0	72.0	36.0	71.5
	(2)	8.3			30.7	3.0	0.1		55.0			35.0	73.5	34.0	72.0

rule. Le Châtelier [23] first applied the rule to the limits of inflammability of gases. The equation for expressing this law in its simplest form is written as follows:

$$L = \frac{100}{\dfrac{P_1}{N_1} + \dfrac{P_2}{N_2} + \dfrac{P_3}{N_3} + \dfrac{P_4}{N_4} +, \text{ etc.}}$$

where P_1, P_2, P_3, P_4, etc., are the proportions of each combustible gas present in the original mixture, free from air and inerts, so that $P_1 + P_2 + P_3 + P_4$, etc. = 100, and N_1, N_2, N_3, N_4, etc., are the lower limits of inflammability of each combustible in air, and L is the lower limit of inflammability of the mixture. The same method can be used for the upper limit.

As an example of the application of this law we may take a natural gas of the following composition:

23 Le Châtelier, H., and Boudouard, O., *Compt. rend.*, **126**, 1344-7, 1510-3 (1898).

HYDROCARBON PRESENT

PERCENT BY VOLUME		LOWER LIMIT
Methane	80.0	5.00
Ethane	15.0	3.22
Propane	4.0	2.37
Butane	1.0	1.86

Lower limit =

$$\frac{80.0}{5.00} + \frac{15.0}{3.22} + \frac{4.0}{2.37} + \frac{1.0}{1.86} = 4.37$$

The limits of inflammability of natural, manufactured, producer, blast-furnace, automobile, and sewage gases may be calculated from a knowledge of the composition of constituents composing the gases and their limits of inflammability.[24] The rather long and complicated procedure is an extension of the original "mixture law," just outlined. As was indicated there, this law is applicable only to mixtures free from inert gases and air, so the $P_1 + P_2 + P_3 +$

24 Jones, G. W., *Chem. Revs.*, **22**, 1-26 (1938).

$P_4 = 100$. The presence of a considerable fraction of inerts such as carbon dioxide, nitrogen, and water vapor in many of the more common industrial gases results in inaccuracies in the calculated limits, and Jones [24] suggested that these inerts could

the 12.4 percent hydrogen, making a total of 18.6 percent; the 53.4 percent nitrogen is combined with the 27.3 percent of carbon monoxide, making a total of 80.7 percent. There being no other inert gases, the 0.7 percent methane is taken alone. Next,
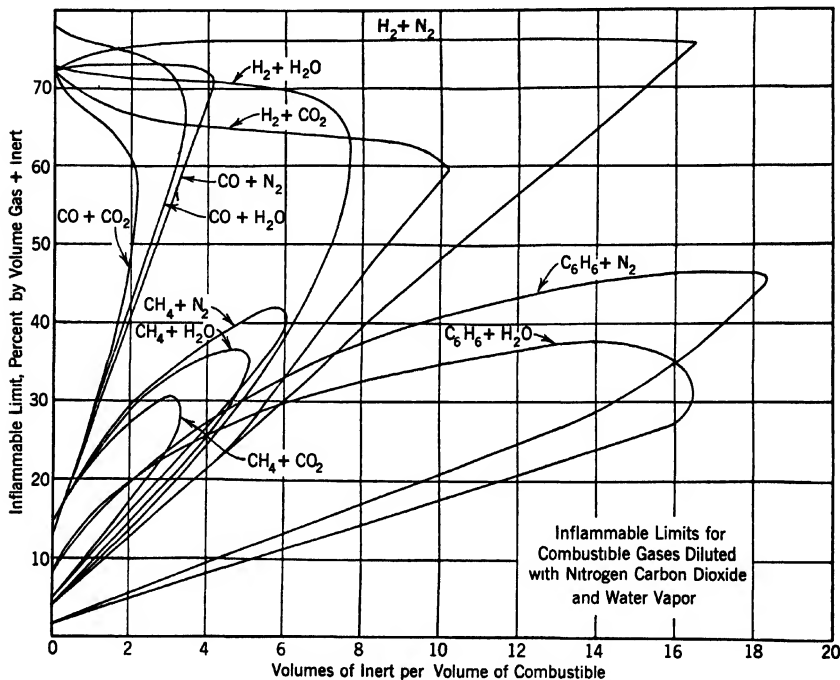
FIG. 10.   Inflammable limits for gas mixtures.[25]

be combined with the combustible constituents, the inflammable limits of these combinations being used in the "mixture law" in place of the limits of the pure gases.

As an example of the application of this law, take a producer gas of the composition shown in Table IX. The inert carbon dioxide and nitrogen may be apportioned with the different combustibles in any one of several ways. In one of these the 6.2 percent carbon dioxide is combined with

the ratio inert to combustible is found for each of the groups, and the explosive limits for each mixture [25] is obtained from Fig. 10 or from the tables published by Jones.[24] Le Châtelier's mixture law is now applied, using the data just obtained as shown in Table IX, and the calculated limits are found to be 19.0 and 70.5 percent, respectively, as compared with the experimentally

25 Yeaw, J. S., and Shnidman, L., *Proc. Am. Gas Assoc.*, **1938, 724.**

determined inflammable limits [26] for this producer gas in air of 20.7 and 73.7 percent.

Table IX shows the analysis of various mixtures of gases for which the explosive limits have been determined and then calculated according to the method just outlined, and these data illustrate the accuracy which may be expected for similar mixtures.

EXPLOSION PRESSURES [27]

When a mixture of gas and air inside a closed chamber is ignited, inflammation proceeds throughout the mixture at a rate depending upon many factors. Heat is produced and pressure develops within the chamber. At the same time some of the heat developed is being absorbed by the unburned gases and by the walls of the vessel itself, thus tending to lower the temperature. At some time during this process these two forces balance, and the pressure ceases to rise. This point is known as the "maximum pressure," and the elapsed time between the initial ignition and the maximum pressure is known as the "time for the explosion." After maximum pressure has been attained, the rate of heat loss to the walls of the vessel is greater than the rate of heat generated within the chamber, and the gas therefore cools and the internal pressure decreases. If the vessel is allowed to cool to its original temperature, the pressure inside the chamber will also become equal to the original pressure, provided that no contraction due to chemical rearrangement has taken place.

Some of the factors which influence the rate of inflammation and the maximum pressure developed include: (1) composition of the combustible gas itself; (2) combustible gas-air ratio in the mixture; (3) physical constants of gas and of air, i.e., densities, specific heats, heat of combustion, heat capacities, etc.; (4) physical constants of the products of combustion, and the changes in these values with temperature; (5) presence of foreign diluents such as water, nitrogen, carbon dioxide, excess oxygen, or argon; (6) size and shape of the explosion vessel; (7) material used for construction of the vessel; (8) surface conditions inside and outside the vessel including the area exposed; (9) initial temperature and pressure of the combustible mixture; (10) position of point of ignition; (11) turbulence in the mixture during inflammation; (12) extent of dissociation of combustion products; (13) heat losses by direct radiation and by conduction; (14) pre-ignition, known as "knock," in which part of the gases is ignited beyond the normal flame front; and (15) "after-burning," in which part of the gases is burned only after maximum pressure has developed.

Various attempts have been made from time to time to calculate the explosion pressures for certain mixtures of combustible gas and air using the fundamental characteristics of the gases. Usually only the simplest types of mixtures have been studied, but even so the results have not been very satisfactory. The number of factors involved in the complex phenomena, and the relative effect of these factors upon the pressures developed, are not sufficiently well known. The application of such methods of calculation to more complex industrial fuels is not feasible at the present time.

From a practical point of view, however, it may not be necessary to consider such methods. Most industrial fuels are composed, in whole or in part, of the combustibles, hydrogen, carbon monoxide, methane, and benzene, and of oil vapors, and in some

[26] Yeaw, J. S., *Ind. Eng. Chem.*, **21**, 1030–3 (1929).

[27] Yeaw, J. S., and Shnidman, L., *Am. Gas Assoc. Monthly*, **21**, 35–6 (1939).

mixtures the inerts nitrogen, carbon dioxide, excess oxygen, or water vapor appear. The explosion pressure curves for mixtures of these pure gases in air are shown in Fig. 11. These curves are quite similar in several

between 100 and 115 pounds per square inch is of minor consequence. The effect of an industrial explosion would be essentially the same regardless of the combustibles, individually or collectively.
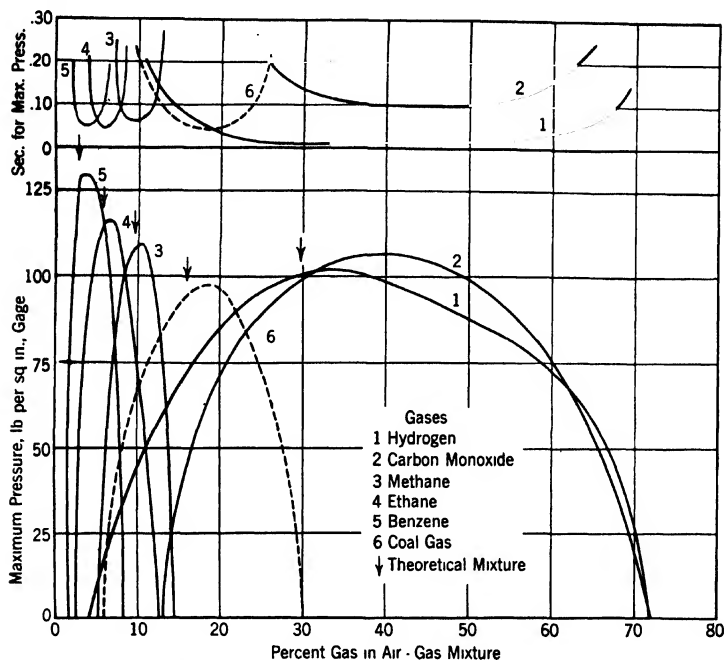
Fig. 11. Explosion times and pressures for mixtures of various gases and air.

characteristics. They all rise very sharply from the lower explosive limit, pass through maxima a little beyond the point of the theoretical combustion mixture, and descend rapidly to the upper explosive limit. Moreover, the maximum pressures developed range from 100 to 115 pounds pressure (gage), with the exception of that for benzene, which rises to 129 pounds per square inch. From a strictly practical standpoint, relative to the possibility of hazardous air-gas mixtures, the difference

Similarly the curves of Fig. 11 showing the time required for the development of the maximum pressures are very much alike. For all practical purposes, the periods of time are almost negligible. The faster-burning gases attain the maximum pressure somewhat more quickly than the slower-burning ones.

In view of the general characteristics of the explosion curves for the various pure gas-air mixtures, it appears that an explosion curve suitable for all practical pur-

poses might be readily predicted when the explosive limits of the gas are known.

Some experimental explosion pressure data for mixtures of certain manufactured gases in air are available in the literature. These gases varied from rich coal gases containing but 2 to 4 percent inerts with a heating value of about 650 Btu per cubic foot to carburetted blue gas containing as high as 40 percent inerts and having a heating value of about 500 Btu per cubic foot. In spite of this fact the maximum explosion pressures ranged between 85 and 95 pounds per square inch. The average explosion pressure curve for these mixtures is shown by the dashed line in Fig. 11.

The proposition that explosion curves suitable for practical purposes could be constructed using the explosive limits of the gas as a starting point is thus reasonable. The estimation of the explosive limits themselves from the analyses of the combustible gas has already been shown to be feasible. The explosion curve for natural gas, which is usually composed largely of methane or of methane and ethane, can be assumed to lie close to those for these two gases, both of which are included in Fig. 11.

There is evidence to indicate that explosion pressures, far in excess of those reported for such experimental tests as those described in this paper, are possible. Abnormal pressures of the order of 300 pounds per square inch have been reported by Grice and Wheeler and by Gleim in their studies of explosions in closed vessels.[28] Henderson has shown in experimental studies using natural gas-air mixtures that pressures approximating 2,000 pounds per square inch were obtained.[29] Peak pressures far in excess of this value were also noted.

FURNACE ATMOSPHERES

The control of furnace atmospheres in the treatment of metals has shown an astounding development since 1930. Coal-gas combustion with limited air supply can furnish an atmosphere with a wide range in its composition. This new use of gas for industrial purposes involves not only its generation but also the control of the furnace atmospheres which protect and surround and react with the metals being treated. Several types of furnace atmospheres that can be obtained from coke-oven gas with varying percentages of air supplied[30] are shown in Table X. For a full and complete discussion of this subject reference should be made to publications of the American Gas Association.[1, 30, 31]

The terms "oxidizing," "neutral," and "reducing" have been applied to furnace atmospheres produced from flue gases. A neutral atmosphere is one in which the sum of carbon monoxide and hydrogen is not more than 0.05 percent and the oxygen is less than 0.05 percent. A reducing atmosphere is one in which the sum of carbon monoxide and hydrogen exceeds 0.05 percent and the oxygen does not exceed 0.05 percent. Oxidizing atmospheres produced by large amounts of excess air in the combustion products have long been known to be required for the baking of cores,[32] the drying of synthetic enamels,[33] and for many

28 Grice, C. S. W., and Wheeler, R. V., *Safety in Mines Research Board (London), Paper* 49 (1929), 26 pp. Gleim, E. J., *U. S. Bur. Mines, Rept. Investigations* 2974 (1929), 6 pp.

29 Henderson, E., *Gas,* 17, No. 9, 23–9 (1941).

30 Anon., *Am. Gas Assoc. Testing Laboratory, Research Bull.* 15 (1942), 110 pp.

31 Anon., *ibid.,* 11 (1940).

32 Campbell, H. L., *The Application of Heat to Core Baking,* Am. Gas Assoc., New York, 1930, 31 pp.

33 Nealey, J. B., *Iron Age,* 136, No. 23, 34–6 (1935). Darrah, W. A., *Oil Paint Drug Reptr.,* 133, No. 6, 36, No. 7, 31, 63, No. 8, 36, 63 (1938). Meyer, K. H., *Steel,* 105, No. 23, 54 (1939).

TABLE X

Typical Furnace Atmospheres [30]

External Heat	Percent Air for Complete Combustion	Percent Gas Constituents						
		Carbon Dioxide	Oxygen	Carbon Monoxide	Hydrogen	Hydro-carbons	Water	Nitrogen
None	100	9.3	0	0	0	0	20.8	69.9
None	95	8.8	0	0.8	1.0	0	20.7	68.7
None	50	3.4	0	10.0	13.1	1.3	18.3	53.9
1,800	15	1.2	0	21.0	47.2	2.2	....	28.4

phases of ceramic work.[34] Reducing atmospheres containing free hydrogen and carbon monoxide as well as some of the hydrocarbons have been employed in chemical processes for the reduction of metals from their ores and are known to be helpful in minimizing scaling of steel,[35] oxidation of copper,[36] etc. Strongly reducing atmospheres are employed for carburizing steel.[37]

Gaseous atmospheres consisting of hydrogen, ammonia, nitrogen, etc., have been used to some extent for a number of years and have found growing application in the metallurgical field. The need for these was fostered by the increasing interest in bright finishes as well as the demands of the automotive industry for a degree of perfection in sheet steel for deep drawing which exceeded previous requirements. Basic data indicating the effect of specific atmospheres upon metals, glazes, paints, etc., have been made available through extensive research.[38]

The effect of various gases, alone and in combination, in the heat treatment of steel has been repeatedly investigated.[35, 39, 40]

34 Hossenlop, A. M., and Russell, R., Jr., *J. Am. Ceram. Soc.*, **18**, 204-5 (1935). Gehrig, E. J., *Am. Gas Assoc. Monthly*, **17**, 466-8 (1935); *Iron Age*, **137**, No. 6, 26-9 (1936). Mackay, A., *Gas J.*, **216**, 148-50 (1936). Dieterichs, W., and Lloyd, P., *ibid.*, **213**, 617-9 (1936). Nealey, J. B., *Iron Age*, **140**, No. 14, 26-8 (1937). Smith, A. J. G., *Gas Age*, **83**, No. 1, 30 (1939). Greaves, R. L., *Gas J.*, **232**, 152-4, 157-8, 163-5 (1940). Brown, L., *Am. Gas Assoc. Monthly*, **23**, 361-2 (1941). Anon., *Ceram. Ind.*, **36**, 55, 58-9 (1941).

35 Murphy, D. W., *Iron Steel Eng.*, **9**, 260-6 (1932); *Trans. Am. Soc. Steel Treating*, **21**, 510-29 (1933). Upthegrove, C., *Univ. Mich. Eng. Research Bull* **25** (1933), 36 pp. Upthegrove, C., and Murphy, D. W., *Trans. Am. Soc. Steel Treating*, **21**, 73 90 (1933). Whiteley, J. H., *J. Iron Steel Inst.*, **131**, 181-99 (1935); *Heat Treating Forging*, **21**, 223-8 (1935); *Engineering*, **139**, 691-4 (1935). Gillett, H. W., *Metals & Alloys*, **6**, 195-207, 235-46, 293-8, 323-7 (1935). Halkett, R., *Gas J.*, **213**, 483-4 (1936). Hotchkiss, A. G., *Metal Progress*, **31**, 375-9 (1937); *Ind. Eng. Chem.*, **33**, 32-8 (1941). Nealey, J. B., *Metals & Alloys*, **9**, 198-200 (1938). Kentnor, C. B., *Gas Age*, **82**, 23-4 (1938). Cline, C. R., and Segeler, C. G., *Ind. Eng. Chem.*, **33**, 46-54 (1941). Keller, J. D., *Mech Eng*, **63**, 507-13 (1941).

36 Tielking, J. W., and Lehrer, W., *Iron Age*, **140**, No. 24, 59, 136-8 (1937). Darrah, W. A., *Ind. Heating*, **4**, 722-6, 1079-80 (1937); *Steel*, **101**, No. 4, 36-42 (1937). Hawkins, R. D., *Proc. Am. Gas Assoc.*, **1938**, 558-65. Hotchkiss, A. G., *Ind. Eng. Chem.*, **33**, 32-8 (1941).

37 Fells, H. A., *Gas J.*, **216**, 335-6 (1936). Roush, R. W., *Steel*, **101**, No. 8, 38-41 (1937). Nealey, J. B., *Machinery (N. Y.)*, **44**, 124-7 (1937-8). Krappe, J. M., *Iron Age*, **147**. No. 15, 47-50, No. 16, 28-31 (1941). Gier, J. R., *Ind. Eng. Chem*, **33**, 38-41 (1941). Darrah, W. A., *ibid.*, **33**, 54-9 (1941). Apter, R. F., and Smith, H. W., Jr., *Am. Machinist*, **86**, 871-4, 947-9 (1942).

38 Marshall, A. L., *Trans. Am. Soc. Metals*, **22**, 605-20 (1934). Austin, J. B., *Ind. Eng. Chem.*, **33**, 23-31 (1941). Conner, R. M., *Am. Gas Assoc. Monthly*, **23**, 361-2 (1941).

39 Smith, A. J. G., *Gas J.*, **215**, 660 (1936). Steever, A. M., *Iron Age*, **140**, No. 15, 78-9 (1937); *Proc. Am. Gas Assoc.*, **1937**, 412-4. Nealey, J. B., *Machinery (N. Y.)*, **44**, 530-3 (1937-8). Trautschold, R., *Steel*, **108**, No. 5, 79-80 (1941).

40 Gillett, H. W., Upthegrove, C., Murphy, D W., and Whiteley, J. H., in ref. 35.

The factors involved are too complex to justify the hope that any one type of protective atmosphere will be "best" for all steels. Principal points to consider apart from the kind of metal being treated are time, temperature, surface area, type of combustion chamber, composition of the atmosphere gas, rate of flow of the atmosphere gas, and sources of contamination.

No definite figures can be given as to the total quantity of controlled atmosphere needed for any particular operation, although it has been found that greater uniformity of results can be obtained by recirculation. This reduces the amount of gas needed and tends to keep the mixture uniform and in equilibrium. It is important to remember the possibility of various reactions between the gaseous components which may lead to the building up of moisture and other harmful constituents under certain conditions of temperature.

Atmospheres and steel treating involve reactions between the various constituents of the gas and the product being treated. At the temperature of the industrial furnace, steel reacts with many gaseous constituents both directly and through secondary reaction products; oxygen, for example, reacts with carbon monoxide to make carbon dioxide and forms iron oxide scale; carbon in the steel may be removed by oxygen, water, and carbon dioxide, as carbon monoxide or carbon dioxide, then fresh carbon from the interior of the metal may diffuse into the decarburized surface areas. These and other reactions may occur simultaneously and, in general, accelerate with rising temperature although steels appear to behave in various ways.

The mechanics and rates of oxidizing effects have been reported by many investigators,[40] who have indicated the various substances causing and influencing scaling. While it is desirable to eliminate or mini-

mize the scaling of the metal surface, other reactions may be occurring at the same time which may be quite as objectionable. Scaling may do no harm if the steel is free scaling.

Scale represents a loss of metal which may or may not be significant, depending upon the type of work involved. For the control of oxidation alone, elimination of water vapor, oxygen, and carbon dioxide and maintenance of suitable reducing conditions are generally sufficient. Unburned gas as well as various partially burned gas mixtures are applied for this type of control.[41] For example, scaling of low-carbon steel can be minimized during low-temperature annealing operations by the use of the flue products from gas combustion, provided that a little decarburization is permitted. The relation between the atmosphere in open furnaces and the scaling of steels is fairly definite. There is little reduction in scale formed by burning city gases to produce up to 6 percent carbon monoxide at furnace temperatures of 2,000° F, that is, with about 77 percent of the air required for combustion.

Scaling of steels at forging temperatures is more difficult to control, particularly as the kind of scale and its adherence as well as the amount must be considered. To eliminate scaling at forging temperatures [11, 12] requires from 14 to 16 percent carbon monoxide, but such atmospheres would entail uneconomic combustion as a rule if the same gas were used for heating as well as for the control of furnace atmosphere. Control of atmosphere for forging [43] has reduced the amount of scale, its thickness, and the extent of decarburization.

The removal of carbon from the surface

41 Jominy, W. E., and Murphy, D. W., *Univ. Mich., Eng. Research Bull.* **21** (1931), 150 pp.

42 See Steever, A. M., in ref. 39.

43 Foster, W., *Metal Progress*, **29**, No. 1, 51–2 (1936).

of steel by carbon dioxide, water vapor, oxygen, and hydrogen tends to produce undesirable skin conditions. Moist hydrogen is particularly active as a decarburizing agent.[44] Nitrogen has also been suggested as a decarburizing agent when moist.

Because of simultaneous scaling and decarburization, the control of one generally requires control of both these actions in order to obtain the desired finished surface condition. A reducing atmosphere scales and decarburizes steel more than a slightly oxidizing atmosphere, such as a flue gas containing about 0.5 percent oxygen and no carbon monoxide or hydrogen. It may not be possible to eliminate the various gases involved in oxidation and decarburization, but balance between the constituents can be obtained by proper control of the furnace atmosphere so that the effects are minimized. The principal interactions between iron and iron carbide and different furnace gases, which produce the two effects which have just been described, are as follows:

No reaction:

$$N_2 \quad + Fe$$
$$H_2 \quad + Fe$$
$$N_2 \quad + Fe_3C$$
$$CH_4 + Fe_3C$$
$$CO \quad + Fe_3C$$

Oxidizing:

$$O_2 \quad + 2Fe \quad \rightleftharpoons 2FeO$$
$$CO_2 + Fe \quad \rightleftharpoons FeO + CO$$
$$H_2O + Fe \quad \rightleftharpoons FeO + H_2$$

Carburizing:

$$CH_4 + 3Fe \quad \rightleftharpoons Fe_3C + 2H_2$$
$$2CO + 3Fe \quad \rightleftharpoons Fe_3C + CO_2$$

Decarburizing:

$$2H_2 + Fe_3C \rightleftharpoons 3Fe \quad + CH_4$$
$$O_2 \quad + 2Fe_3C \rightleftharpoons 6Fe \quad + 2CO$$
$$CO_2 + Fe_3C \rightleftharpoons 3Fe \quad + 2CO$$
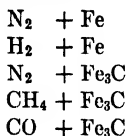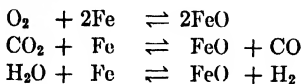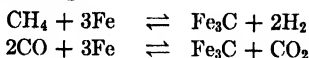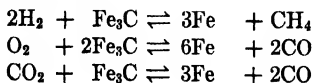
The addition of alloying elements to the iron and carbon will greatly enlarge the number of possible reactions, so that this list cannot be taken as complete but merely as illustrative of the difference in behavior between the various combinations of materials present in industrial furnaces, depending upon the particular circumstances of time, temperature, and concentration which are involved. The possibility of catalyzing effects, especially in the reactions favored by the presence of moisture, needs to be considered in practice.

The combustion products themselves can interact in accordance with the well-known equations given below:

$$2H_2 + O_2 \rightleftharpoons 2H_2O$$
$$2CO + O_2 \rightleftharpoons 2CO_2$$
$$CH_4 + H_2O \rightleftharpoons CO + 3H_2$$
$$2CO \rightleftharpoons CO_2 + C$$
$$C + H_2O \rightleftharpoons CO + H_2$$
$$CO_2 + H_2 \rightleftharpoons CO + H_2O$$
$$CH_4 \rightleftharpoons C + 2H_2$$
$$N_2 + O_2 \rightleftharpoons 2NO$$
$$2NO + O_2 \rightleftharpoons 2NO_2$$
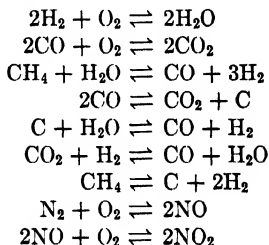
The first two equations, showing the dissociation equations for water vapor and carbon dioxide, occur in all combustion reactions, in the presence of iron at elevated temperatures. The equilibrium values for various partial pressures are available.[3] The fourth equation is frequently considered in its reverse aspect, but, in the presence of heated iron oxide, carbon monoxide can decompose as indicated. The fifth equation represents the water-gas reaction, the constants for which are given in the reference just cited. This, as well as the reactions showing the simple cracking of methane, is distinctly catalyzed by the presence of hot iron oxides.

Minimum decarburization in direct-fired

44 Jominy, W. E., *Trans. Am. Soc. Metals*, **24**, 96–125 (1936).

furnaces requires (1) a fuel low in hydrogen; (2) a positive furnace pressure; (3) a slightly oxidizing combustion adjustment with proper mixing; (4) the minimum time and temperature; and (5) pieces as near cubes as possible to reduce decarburized area and hence decarburized depth in finished work.

It is important to understand the factors involved in decarburization because it cannot be prevented by expensive special atmosphere equipment alone. Oxygen, carbon dioxide, and water are the chief offenders, but it is just as necessary to prevent their formation as to provide for their removal. Both carbon dioxide and water will re-form if oxygen gets in, and there are many oxygen sources: air leakage, dissolved oxygen in wash water, scale and rust on the work, oils, and moisture on the work.

Protective furnace atmospheres have been used for the treating of copper and its alloys.[46] Copper behaves differently from steel because of the reaction between these elements and the constituents of the protective atmospheres. Copper is extremely sensitive to the presence of oxygen and sulfur. Hence, a slightly reducing atmosphere is recommended with very low sulfur content. Copper wire annealing as well as bright annealing has been successfully carried out. Protective furnace atmospheres made from coal gas have likewise been employed for other nonferrous metals as in silver treating and annealing, nickel treating, as well as many nickel alloys.[45]

Other Industrial Applications

Coal gas has likewise been a source for inert gas[46] by controlled combustion to yield a gas low in oxygen and combustibles and consisting mainly of carbon dioxide and nitrogen. Such inert gases are used rather extensively not only in the gas industry but also in other industries as a means of purging various types of equipment, such purging operations insuring safety in removing from service or putting into service equipment that contains combustible gases or vapors.[47] Inert atmospheres have also been used for protection against fire and explosion hazards in storing of solvents and chemicals in paint industries, and in the protection of chemical processes. The principles outlined for the use of inert gas as a safety measure have been described in detail in the literature.[47]

Other developments in gas utilization include the successful baking and drying of metal finishes by gas heating equipment,[48, 18] the continuous bright annealing of wire in open flames without furnaces or special atmospheres,[49] and the application of gas drying to new inks for high-speed printing.[50] The first reports of the successful use of oxygas flame hardening, as distinct from oxyacetylene, were released in the United States.[51] Specialized new equipment was developed in several fields, notably the double-boiler application for melting zinc[52] and a new process for corrosion-proofing of iron and steel.[53]

45 Ross, F. W., *Iron Age*, 141, No. 13, 30–3 (1938). Halkett, R., *Gas J.*, 213, 483–4 (1936).

46 Smith, H. W., *Gas*, 16, No. 3, 24–7 (1940); *Gas J.*, 229, 304 (1940).

47 Alrich, H. W., *Proc. Am. Gas Assoc.*, 1932, 826–38. Tomkins, S. S., *ibid.*, 1934, 799–822. Yeaw, J. S., and Shnidman, L., *ibid.*, 1938, 717–40.

48 Weller, H. C., *Am. Gas Assoc. Monthly*, 18, 194–6 (1936). Mann, C. P., *Metal Finishing*, 39, 457–60 (1941).

49 Anon., *Machinery* (*N. Y.*), 46, 272–3 (1939).

50 Wilson, R. P., *Proc. Am. Gas Assoc.*, 1939, 370–1.

51 See Apter, R. F., and Smith, H. W., Jr., in ref. 37.

52 Mann, R. F., *Am. Gas J.*, 150, No. 1, 25–8, 50, 52, No. 2, 15–8 (1939). Carlson, F. M., *Metal Ind.*, 37, 577–9 (1939).

53 Mann, R. F., *Am. Gas J.*, 148, No. 6, 17–20 (1938).

An important application of coal gas is in the production of power using the combustion gas turbine.[54] The gas combustion turbine has had a long history, but only in the past decade has it shown any noticeable advance. The development of the gas turbine was retarded by the lack of accurate knowledge of the thermodynamics of gas combustion, of available materials capable of withstanding the physical and chemical reactions of the combustion of gas at temperatures from 1,000 to 1,100° F, and of an air compressor with sufficiently high adiabatic efficiency. In the present gas turbine, as applied to power generation, air

54 Marks, L. S., and Danilov, M., *Trans. Am. Soc. Mech. Engrs.*, **46**, 1095 128 (1924). Meyer, A., *Proc. Inst. Mech. Engrs. (London)*, **141**, 197–212 (1939) ; *Mech. Eng.*, **61**, 645–52 (1939). Northfield, H. J., *Engineer*, **167**, 406 (1939). Rettaliata, J. T., *Power*, **83**, 732–4 (1939), **85**, 266–7 (1941) ; *Engineer*, **170**, 63–4, 78–9 (1940). Tucker, S. A., *Power*, **83**, 316–9 (1939). Anon., *Engineering*, **147**, 186–8 (1939) ; *Mech. Eng.*, **61**, 312–3 (1939), **62**, 744–5 (1940) ; *Ry. Mech. Eng.*, **114**, 144–8 (1940) ; *Ry. Age*, **108**, 588–90 (1940) ; *Power Plant Eng.*, No. 6, **45**, 65–8 (1941).

is compressed to some 60 pounds per square inch and 370° F. It then enters a combustion chamber where about 25 percent passes to the gas burner and 75 percent is bypassed around the burner to dilute the products of combustion and reduce the temperature of the mixture to around 1,000° F. The gas is then expanded through six or seven reaction stages, leaves at a temperature of around 600° F, and is discharged to the atmosphere. This exhaust heat can be utilized at the expense of a small back-pressure for preheating the combustion air leaving the compressor. The overall thermal efficiency of the gas compressor set is about 17 percent, and if an air preheater is included, this efficiency would be increased to around 21 percent. The present thermal efficiency of the gas turbine is limited by the permissible temperatures with available turbine materials. It is not high enough to be attractive for primary power generation. The gas turbine with its rapid starting abilities has possibilities for standby and peak-load service.

THE CHEMICAL NATURE OF COAL TAR

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Coal tar is one of the primary products resulting from the destructive distillation or carbonization of certain kinds of coal at temperatures above 450° C in suitable equipment from which oxygen is excluded. The other primary products are coke, aqueous liquor, light oil, and gas. The three variables mentioned, namely, kind of coal, carbonization temperature, and type of carbonizing equipment, determine the yields and the physical and chemical characteristics of the coal tar and of the other primary products as well.

Effect of Kind of Coal Carbonized

In all countries where coal is carbonized commercially, the principal kind of coal used is the common banded type or variety of bituminous coal. In the United States, coal carbonization is limited entirely to this rank and type, except for one small installation in North Dakota that carbonizes lignite. Germany, in addition to bituminous coal, carbonizes large quantities of brown coal, a type of lignitic coal. In Scotland some bituminous coal of the splint type is used in blast furnaces in place of coke; although this is not coal carbonization in the sense that coke is recovered as a primary product, it is mentioned here because the destructive distillation of splint coal in a blast furnace produces so-called blast-furnace tar, a type of coal tar.

Anthracitic coals are not carbonized commercially. When destructively distilled they do not fuse to form coke, and they yield practically no tar or light oil and only minor quantities of gas.

Bituminous coals, of the splint, cannel, and boghead varieties, unlike the common banded type, do not fuse to form coke and, with the exception of the use for splint coal in Scottish blast furnaces mentioned above, are not carbonized commercially. Formerly cannel and boghead coals were destructively distilled to obtain "coal oil" for illuminating purposes, but the use of electricity, petroleum oils, and gas has caused the production of coal oil for this purpose to be discontinued.

Subbituminous coals usually are not carbonized commercially because of their poor coking qualities or because they are not produced or marketed in commercially important quantities.

Lignitic coals are carbonized to some extent by low-temperature methods, especially in Germany, to obtain a friable char that may be used as such or in briquet form for fuel purposes. The low-temperature lignitic char is sometimes mixed with high-volatile bituminous coal that is carbonized at high temperatures.

Table I, in which coals are arranged vertically by rank, according to Standard D388-38, and horizontally by type or vari-

TABLE I

CARBONIZING CHARACTERISTICS OF COALS OF DIFFERENT RANK AND TYPE

Classification of Coals by Rank A.S.T.M. Designation D388-38	Classification of Bituminous and Subbituminous Coals by Varieties (Types) A.S.T.M. Designation D493-39			
	Common Banded Coal	Splint Coal	Cannel Coal	Boghead Coal
I Anthracitic	Anthracites are not carbonized commercially They have progressed so far in degree of coalification that when destructively distilled they yield practically no tar or light oil and only minor quantities of gas. They do not fuse to form coke. Because of their high degree of coalification, different varieties of anthracites are not readily distinguishable or significant.			
II Bituminous	Carbonized commercially by high- and low-temperature processes Fuse to form coke and yield commercial quantities of tar, light oil, and gas.	Not carbonized commercially. Do not fuse to form coke. Because lumps retain shape and strength, used in some Scottish blast furnaces in place of coke; source of Scottish blast-furnace tar.	Not now carbonized commercially. Do not fuse to form coke Formerly distilled to obtain "coal oil" for illumination. Char used as fuel in process or wasted.	Not commercially carbonized. Formerly processed like cannel coal to obtain "coal oil."
III Subbituminous	Usually not carbonized commercially, because of poor coke quality, although produced and marketed in commercially important quantities.	Not carbonized commercially because not produced or marketed in commercially important quantities and because of poor coking qualities.		
IV Lignitic	Carbonized by special low-temperature methods. Do not fuse to form coke but form friable char used as such or briquetted. High yields of tar and light oil of low-temperature variety. Gas is of poor quality. Lignitic coals are not ordinarily distinguished commercially as to variety.			

ety, according to Standard D493-39 of the American Society for Testing Materials, summarizes the above information.   The areas representing coals of bituminous rank, common banded variety, and coals of lignitic rank are bordered by heavy lines to distinguish them from the coals of other ranks and types which are not carbonized commercially.

Bituminous or coking coals of the common banded variety are further subdivided, according to rank or fixed-carbon content, as follows: high-volatile A, high-volatile B

and C, medium-volatile, and low-volatile. Fieldner and Davis [1] have shown that the yield of coke obtained from a given bituminous coal is closely proportional to the rank of the coal as measured by its fixed carbon or volatile matter. However, the results of the U. S. Bureau of Mines-American Gas Association Coal Carbonization Tests reported in *Monograph* 5 [2] have

[1] Fieldner, A. C., and Davis, J. D., *Proc. 3rd. Intern. Conf. Bituminous Coal*, 1, 540–86 (1931).
[2] Fieldner, A. C., and Davis, J. D., *U. S. Bur. Mines, Monograph* 5 (1934), 164 pp.

shown that yields of tar are not inversely proportional to the rank of the coal or volatile matter as might be assumed, except with certain reservations.

A systematic attempt to analyze the data from these tests and also from tests by Yancey, Johnson, and Selvig [3] has been made by Parry.[4] He stated that:

in correlating the total yield of tar from any carbonizing system with the proximate analysis of the coal, a better relationship should be shown with the volatile matter exclusive of oxygen than with volatile matter alone · · · . The yield of tar is a function of the square of the oxygen-free volatile matter for all temperatures of carbonization. Consequently, the general relationship may be stated by the equation:

Tar yield, in percent of coal = CV^2

where V is percentage of oxygen-free volatile matter and C is a constant whose value is governed by the size and shape of the retort and the temperature of distillation.

The Bureau of Mines-American Gas Association data have been treated mathematically by Lowry, Landau, and Naugle.[5] On the basis that "the distinction between tar and light oil is based largely on volatility and the distribution is at least partly dependent on the efficiency of scrubbers and cooling towers," they combined tar and light oil values $(T + LO)$ in their correlations. They found that

$$(T + LO) = a + b(VM) + c(H_2O)$$

and correlated the constants a, b, and c with the temperature of carbonization as follows:

$$a = -17.13 + 0.03166T - 0.1656 \times 10^{-4}T^2$$

$$\log b = \frac{498.7}{T + 273} - 0.9411$$

$$c = 0.00004T - 0.242$$

Lowry, Landau, and Naugle stated that "it should be emphasized that the moisture content is not considered as having any direct effect on the $(T + LO)$ but is used in the equation solely as an index of rank of the coal." They preferred the values a, b, and c found from the above equations to a', b', and c' which were determined by least squares for the data obtained at the individual temperatures. All the values used in their calculations for tar plus light oil $(T + LO)$ are given in Table II.

The same authors also correlated light oil (LO) with the volatile-matter content of the coal by means of the equations

$$(LO) = a + b(VM)$$

where b is related to temperature by the equation

$$\log b = -0.5844 - \frac{1,100}{T + 273}$$

Table III contains the values used in their calculations, the items having the same significance as in Table II except that values of a were developed to give zero errors when using b calculated by the equation relating it to temperature.

Whereas Parry and also Lowry, Landau, and Naugle have shown that there is a relationship between the *yield of tar* and the volatile matter of the coal carbonized, particularly when the oxygen or the moisture content of the coal is taken into consideration, no such direct relationship can be established between the *properties of the tar* produced and the volatile matter of the coal carbonized. That this is especially true when the coal is carbonized under high-temperature conditions is shown by Table IV, which lists some of the proper-

[4] Parry, V. F., *U. S. Bur. Mines, Rept. Investigations* 3482 (1940), 37 pp.

[5] Lowry, H. H., Landau, H. G., and Naugle, L. L., *Trans. Am. Inst. Mining Met. Engrs.*, 149, 297–330 (1942).

[3] Yancey, H. F., Johnson, K. A., and Selvig, W. A., *U. S. Bur. Mines, Tech. Paper* 512 (1932), 94 pp.

TABLE II

Yield of Tar plus Light Oil $(T + LO)$

$$(T + LO) = a + b(VM) + c(H_2O)$$

Temperature, °C	500°	600°	700°	800°	900°	1,000°	1,100°
n	45	48	45	50	83	46	17
$(T + LO)$, avg., percent	8.2	8.4	7.6	7.2	6.7	6.1	5.4
$(T + LO)$, max., percent	12.7	11.8	12.0	11.0	9.3	8.9	7.8
$(T + LO)$, min., percent	1.6	1.8	1.9	2.2	1.6	1.7	1.1
R	0.96	0.96	0.96	0.96	0.95	0.97	0.95
a'	−5.25	−4.17	−3.21	−2.35	−2.01	−1.94	−2.45
b'	0.447	0.427	0.375	0.331	0.304	0.281	0.267
c'	−0.158	−0.202	−0.223	−0.211	−0.208	−0.199	−0.204
PE, percent	0.61	0.59	0.50	0.42	0.35	0.33	0.35
E, max., percent	+2.1	+1.6	+1.6	+1.4	+1.4	+1.1	+1.1
E, max., percent	−2.1	−1.7	−1.6	−1.4	−1.1	−1.2	−0.7
a		−4.10	−3.09	−2.41	−2.06	−2.04	−2.35
b		0.427	0.373	0.334	0.305	0.282	0.264
c		−0.218	−0.214	−0.210	−0.206	−0.202	−0.198

n = number of coals for which data were averaged.
R = correlation coefficient.
a', b', and c' = constants for equation determined by method of least squares for data obtained at the individual temperature.
PE = probable error in percentage.
E, max. = maximum positive and negative errors, calculated - observed.
a, b, and c = constants obtained from the equations relating them to temperature for temperatures from 600° C to 1,100° C.

TABLE III

Yield of Light Oil

$$(LO) = a + b(VM)$$

Temperature, °C	500°	600°	700°	800°	900°	1,000°	1,100°
n	40	42	41	44	78	43	19
(LO) avg., percent	0.31	0.46	0.63	0.75	0.95	0.94	0.93
(LO) max., percent	0.51	0.73	1.00	1.10	1.33	1.40	1.24
(LO) min., percent	0.11	0.23	0.25	0.40	0.45	0.32	0.28
R	0.75	0.58	0.85	0.82	0.84	0.93	0.91
a'	−0.020	0.093	−0.034	0.044	−0.049	−0.214	−0.338
b'	0.0107	0.0120	0.0213	0.0226	0.0325	0.0374	0.0390
PE, percent	0.046	0.082	0.063	0.076	0.076	0.074	0.073
E, max., percent	+0.19	+0.36	+0.18	+0.34	+0.27	+0.29	+0.20
E, max., percent	−0.12	−0.22	−0.21	−0.24	−0.30	−0.26	−0.16
a	0.008	0.022	0.029	−0.018	0.028	−0.158	−0.410
b	0.0098	0.0143	0.0193	0.0246	0.0300	0.0356	0.0412

ties of thirty high-temperature (900° C) tars arranged in the order of decreasing fixed carbon of the coals from which they were derived.[6] Commenting on this table, Fieldner and Davis concluded that "these high-temperature tars exhibit no systematic variations in properties with rank of coal."

Referring to the fact that "low-temperature tars of the low-rank coals tend to run higher in tar acids and paraffins than those of high rank," whereas this trend is not shown by the thirty high-temperature tars listed in Table IV, Fieldner and Davis concluded that "evidently the thermal decomposition of primary tars at the higher temperatures equalizes their properties." This is well illustrated by Tables V and VI, compiled by C. H. Fisher from data of the U. S. Bureau of Mines.[2] Table V lists the properties of tars produced at 600° C arranged in order of decreasing fixed carbon in the coal. Table VI lists the same properties for tars produced at 1,000° C from the same coals and arranged in the same order of decreasing fixed-carbon content.

Tables V and VI also support the statement by Gluud and Jacobson[7] that "only the composition of true primary tar which has not been overheated is dependent on the coal from which it is recovered by distillation. The composition of all other tars is dependent solely on the effects of decomposition. By decomposition, the differences existing between tars obtained from different coals, such as steam or bituminous, may be eliminated to a great extent." In this same connection Gluud and Jacobson[8] quoted F. Fischer as saying that "the examination of tar reflects the composition

of a coal in about the same proportion as the smoke from a burning library would reflect the nature of the contents of the burning volumes."

Porter,[9] in discussing the effect of coal composition on the properties of coal tar, stated that "the higher oxygen coals give somewhat thinner and less degraded tars with higher content of phenols," and he suggested that "this may be due, in part, to their property of producing, in carbonization, a large proportion of carbon dioxide and water vapor." Granting that the tendency noted by Porter is correct, his suggested explanation would indicate that the direct cause of the differences noted in the properties of tars from high- and low-oxygen coals was temperature and the indirect cause was coal composition.

In general, the effects of coal composition on the yield and properties of tar obtained from coal by carbonization may be summarized as follows:

1. The *yield* of coal tar at all temperatures is influenced by the rank of the coal carbonized.

2. The *nature* of the coal tar is influenced appreciably by the composition of the coal carbonized when carbonization is effected at low temperatures, but, under high-temperature carbonizing conditions, the influence of coal composition is largely or entirely overcome by the thermal decomposition of compounds which caused the tars produced at lower temperatures to have characteristic differences.

EFFECT OF CARBONIZATION TEMPERATURE

The temperature of carbonization, to a greater degree than any other single factor, determines the yield and properties of coal tar and of each of the other primary prod-

6 See p. 75 of ref. 2.

7 Gluud, W., and Jacobson, D. L., *International Handbook of the By-Product Coke Industry*, Chemical Catalog Company, New York, 1932, p. 91.

8 See p. 83 of ref. 7.

9 Porter, H. C., *Coal Carbonization*, Chemical Catalog Company, New York, 1924, p. 326.

TABLE IV

Variation of Properties of 900° C Tars with Rank of Coal [6]

(Tars arranged in order of decreasing fixed carbon in coal)

Coal No.	Dry Tars					Percent of Neutral Oil		Fixed Carbon of Coal—Dry, Mineral-Matter-Free	Btu of Coal—Dry, Mineral-Matter-Free
	Specific Gravity	Btu per Pound	Tar Acids	Neutral Oils	Residue	Aromatics	Paraffins		
			percent	percent	percent			percent [*]	
23	1.18	16,380	3.9	20.8	64.2	88.8	2.2	84.1	15,844
26	1.16	16,570	2.7	24.2	69.6	81.7	11.1	78.6	15,763
4	1.15	16,390	5.2	32.2	59.4	78.7	1.1	76.0	15,742
27	1.18	16,510 .	3.0	20.7	70.2	83.9	6.8	72.5	15,682
11	1.15	16,440	5.1	32.2	59.6	88.7	2.3	71.3	15,510
5	1.16	16,340	9.1	40.0	47.7	81.2	0.4	70.2	15,590
25	1.11	16,430	11.5	39.7	45.5	77.4	12.1	70.0	15,494
8	1.20	16,330	2.9	19.4	69.9	83.8	1.1	69.1	15,642
7	1.21	16,270	2.0	22.8	64.8	81.8	trace	67.7	15,494
17	1.17	16,440	5.6	29.6	58.9	82.9	5.1	67.0	15,529
18	1.16	16,460	7.4	28.6	60.1	78.5	9.5	66.6	15,502
29	1.14	16,330	7.5	29.9	57.4	82.1	7.4	66.1	15,411
24	1.13	16,420	9.2	37.3	50.7	80.5	7.2	65.4	15,375
6	1.17	16,320	7.7	36.5	50.1	79.0	0.5	64.8	15,347
30	1.15	16,380	6.6	29.9	58.4	82.6	6.7	64.3	15,424
9	1.23	16,210	2.5	17.2	70.3	86.6	1.7	63.5	15,480
12	1.17	16,290	4.9	27.3	62.2	88.5	2.2	63.5	15,426
1	1.13	.	6.8	21.3	69.9	.	...	63.0	15,310
28	1.15	16,390	7.7	32.1	55.6	81.6	7.1	62.6	15,338
3	1.15	16,380	6.8	30.2	62.1	82.9	3.6	62.3	15,497
13	1.16	16,320	8.7	33.8	54.4	78.8	8.2	62.0	15,090
2	1.16	16,310	6.5	24.8	66.4	.	...	61.9	15,092
14	1.15	16,350	7.9	33.7	54.1	78.0	9.0	61.6	15,236
20	1.15	16,310	9.9	35.2	51.8	79.8	8.4	60.8	15,270
10	1.17	16,220	7.5	29.8	55.1	81.3	1.4	60.6	14,690
22	1.13	16,360	10.2	35.5	51.5	79.5	9.5	59.9	15,307
15	1.16	16,360	6.7	34.6	53.3	82.2	6.3	59.5	15,201
16	1.18	16,300	5.1	26.7	62.1	86.5	3.6	58.9	15,325
19	1.15	16,270	6.5	34.9	51.5	82.3	2.7	57.1	14,677
21	1.17	16,090	7.7	29.0	55.9	81.0	1.7	57.0	14,500

[*] Dry, mineral-matter-free fixed carbon = $\dfrac{100 \times \text{Dry fixed carbon}}{100 - (1.1 \times \text{Dry ash})}$.

TABLE V

ANALYSIS OF DRY TAR PRODUCED AT 600° C *

Coal No. †	Specific Gravity 15.6°/15.6° C	Heating Value, Btu per pound	Tar Yield, Percent by Weight of Coal as Carbonized	Ultimate Analysis, Percent by Weight						Boiling Range, °C, Percent by Volume					Distillate, Percent by Volume of Dry Tar			Neutral Tar Oil, Percent by Volume		
				Carbon	Hydrogen	Nitrogen	Oxygen	Sulfur	Free Carbon	0-170	170-235	235-270	270-350	Residue	Tar Acids	Tar Bases	Neutral Oil	Olefins	Aromatics	Saturates
23	1.10	16,930	1.6	89.3	7.0	0.6	2.6	0.5	1.0	6.4	11.4	8.2	16.9	57.1	4.5	0.7	37.7	6.5	80.2	13.3
4	1.07	16,880	4.1	87.5	7.5	0.7	3.7	0.6	0.6	6.4	17.5	7.7	29.5	38.8	11.8	1.9	37.5	9.2	86.5	4.3
11	1.05	17,020	5.9	86.6	8.1	0.7	4.1	0.5	1.0	8.3	19.9	10.1	20.2	41.5	12.6	0.5	45.4	8.0	65.6	26.4
17	1.04	16,950	8.4	85.6	8.4	0.9	4.8	0.3	0.8	6.7	20.8	7.7	21.9	42.9	16.2	1.3	39.6	12.0	51.5	36.5
9	1.09	16,460	10.3	85.7	7.3	1.0	5.5	0.5	4.8	4.7	21.6	7.9	19.7	46.1	15.8	0.6	37.4	16.2	66.9	16.9
12	1.06	16,630	9.9	85.3	8.2	0.9	5.1	0.5	2.1	6.9	21.2	8.6	21.3	42.0	16.2	0.5	41.3	10.4	60.7	28.9
3	1.04	16,740	9.0	86.0	8.4	0.9	4.3	0.4	1.3	11.9	20.6	11.3	9.9	46.3	16.7	0.8	36.2	14.1	67.8	18.1
14	1.04	16,820	10.3	85.2	8.7	0.8	5.0	0.3	2.2	6.0	21.1	10.8	22.3	39.8	17.3	0	42.9	9.5	54.6	35.9
22	1.04	16,640	10.9	84.0	8.3	0.8	6.5	0.4	1.2	6.4	23.1	9.3	21.7	39.3	20.3	1.5	38.9	12.8	55.0	32.2
19	1.04	16,820	9.8	84.2	8.6	0.8	5.9	0.5	1.4	5.5	21.6	10.7	23.9	38.3	17.5	1.7	42.5	14.5	52.8	32.7

* Tars arranged in order of decreasing fixed carbon in coal. i.e., in order of decreasing degree of coalification.   † Number used in ref. 2 to designate the parent coal.

TABLE VI

ANALYSIS OF DRY TAR PRODUCED AT 1,000° C *

Coal No. †	Specific Gravity 15.6°/15.6° C	Heating Value, Btu per pound	Tar Yield, Percent by Weight of Coal as Carbonized	Ultimate Analysis, Percent by Weight						Boiling Range, °C, Percent by Volume					Distillate, Percent by Volume of Dry Tar			Neutral Tar Oil, Percent by Volume		
				Carbon	Hydrogen	Nitrogen	Oxygen	Sulfur	Free Carbon	0-170	170-235	235-270	270-350	Residue	Tar Acids	Tar Bases	Neutral Oil	Olefins	Aromatics	Saturates
23	1.19	16,450	1.3	91.1	5.6	1.1	1.6	0.6	5.4	1.0	5.4	7.0	16.5	70.1	1.4	0.9	18.3	10.6	88.2	1.2
4	1.18	16,335	4.3	90.1	5.9	1.1	2.1	0.8	6.5	1.7	7.8	6.9	18.3	65.2	3.3	1.2	27.3	23.0	76.7	0.3
11	1.18	16,390	4.6	90.3	5.7	1.1	2.3	0.6	7.2	3.1	11.9	6.3	14.0	64.7	3.4	0.4	27.3	10.3	88.6	1.1
17	1.19	16,410	5.0	91.1	5.6	1.1	1.8	0.4	8.2	2.8	14.0	5.1	12.8	65.3	3.5	1.2	21.7	11.9	84.4	3.7
9	1.24	16,000	6.3	89.9	5.0	1.3	3.1	0.7	22.9	1.3	7.7	3.6	9.0	78.4	1.5	1.2	11.5	13.6	85.5	0.9
12	1.19	16,320	6.3	89.9	5.7	1.3	3.1	0.6	11.5	2.7	15.2	4.2	13.2	64.7	3.4	0.9	24.6	11.3	83.8	4.9
3	1.15	16,390	6.5	89.4	6.5	1.1	2.5	0.5	7.3	5.8	18.0	6.6	6.3	63.3	6.4	1.0	29.2	16.9	81.8	1.3
14	1.16	16,460	6.7	88.9	6.1	1.1	3.4	0.5	6.8	3.9	18.5	5.0	15.4	57.2	6.5	0.9	31.3	9.5	83.6	6.9
22	1.15	16,330	8.0	88.8	6.0	1.1	3.6	0.5	6.7	5.2	16.9	5.7	14.8	57.4	6.5	1.8	29.8	10.6	84.3	5.1
19	1.17	16,335	5.8	89.5	5.8	1.0	3.1	0.6	9.0	3.2	17.3	6.0	15.7	57.8	3.8	2.1	28.9	15.2	82.5	2.3

* Tars arranged in order of decreasing fixed carbon of coal.   † Numbers used in ref. 2 to designate the parent coal.

ucts derived from a given coal when it is destructively distilled.

Table VII, compiled from data published by the U. S. Bureau of Mines,[2]

shows to what extent the yield of each of the primary products, and also the yield of each constituent of each primary product, is influenced by changes in carbonization temperature from 500 to 1,100° C. The tests from which these data were obtained were all performed in a single type and size of experimental retort (13-inch diameter by 26 inches high), and with only

one kind of coal (Pratt). The changing yields of the primary products with increasing carbonizing temperatures are plotted individually in Fig. 1 and collectively in Fig. 2. The curves in these two figures are plotted from the data presented in Table VII. From the curves in these figures, it is obvious that the yield of coke is highest at 500° C, decreases to a minimum at
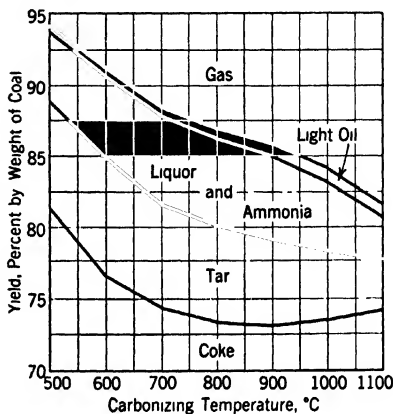
FIG. 2. Effects of carbonizing temperatures on yields of primary products from Pratt coal. Yields of primary products plotted collectively.

900° C, and rises slightly thereafter to 1,100° C. The yield of tar is greatest at 600° C and decreases gradually thereafter. Liquor plus ammonia increases to 700° C, remains substantially constant between 700 and 900° C, and then decreases. Light oil does not vary greatly but reaches a maximum at 1,000° C. Gas increases throughout the entire range.

In commenting on the shape of the tar curve, Fieldner and Davis[10] stated that "the bend in the tar curve is characteristic only for medium- and low-volatile coals. These coals evolve gases and vapors at a lower rate than high-volatile coals, thus

10 See p. 24 of ref. 2.

TABLE VII

YIELDS OF PRIMARY PRODUCTS AND THEIR CONSTITUENTS IN PERCENT BY WEIGHT OF COAL
RESULTING FROM THE CARBONIZATION OF PRATT COAL AT TEMPERATURES OF 500 TO 1,100° C [2]

Carbonization Temperature		500°	600°	700°	800°	900°	1,000°	1,100°
Gas	Carbon dioxide	0.65	0.96	1.36	0.75	0.97	1.18	0.88
	Illuminants	0.47	0.76	1.74	2.02	2.41	2.16	2.41
	Oxygen	0.14	0.14	0.17	0.15	0.25	0.20	0.29
	Hydrogen	0.12	0.34	0.79	1.19	1.41	1.83	2.29
	Carbon monoxide	0.19	0.55	1.14	1.60	2.13	2.99	4.81
	Methane	2.52	4.35	5.38	5.87	6.31	6.99	6.15
	Ethane	1.34	1.32	1.26	0.97	0.31	0.14	0.06
	Nitrogen	0.27	0.38	0.56	0.45	0.61	0.61	0.91
	Total	5.70	8.80	12.40	13.00	14.40	16.10	17.80
Light oil	Olefins	0.05	0.08	0.09	0.07	0.05	0.04	0.03
	Naphthalene	Trace	0.0005	0 00	0.001	0.0008	0.0009	0.002
	Benzene	0.02	0.03	0.10	0.26	0.51	0.63	0.56
	Toluene	0.02	0.04	0.10	0.19	0.16	0.14	0.10
	Paraffins	0.18	0.17	0.07	0.06	0.02	0.02	0.01
	Solvent naphtha	0.11	0.14	0.15	0.11	0.09	0.07	0.05
	Total	0.38	0.46	0.51	0.69	0.83	0.90	0.75
Liquor and ammonia	Ammonia	0.01	0.06	0.20	0.20	0.17	0.16	0.11
	Liquor	4.80	5.70	6.00	5.90	5.70	4.70	2.90
	Total	4.81	5.76	6.20	6.10	5.87	4.86	3.01
Tar	Acids	1.30	1.36	1.11	0.62	0.34	0.18	0.08
	Bases	0.11	0.11	0.12	0.11	0.105	0.06	0.04
	Olefins	0.32	0.40	0.28	0.26	0.25	0.18	0.1'.
	Aromatics	1.53	1.71	1.77	1.76	1.71	1.26	0.82
	Paraffins and naphthenes	1.43	1.22	0.45	0.15	0.105	0.06	0.03
	Residue above 350° C	2.91	3.60	3.57	3.90	3.59	3.26	2.46
	Total	7.60	8.40	7.30	6.80	6.10	5.00	3.60
Coke	Ash	9.20	8.20	8.60	9.00	9.20	9.50	9.30
	Hydrogen	2.50	1.80	1.20	0.80	0.50	0.30	0.20
	Carbon	64.90	63.00	61.70	61.40	61.60	62.10	63.30
	Nitrogen	1.50	1.30	1.10	1.00	1.10	1.00	0.60
	Oxygen	2.60	1.80	1.10	0.70	0.10	0.00	0.20
	Sulfur	0.60	0.50	0.70	0.50	0.60	0.50	0.50
	Total	81.30	76.60	74.40	73.40	73.10	73.40	74.10

permitting more cracking of tar into gas and coke. High-volatile coals gave a greater yield of tar at 500° than at 600°, provided the tar offtake was kept heated near the carbonizing temperature to prevent refluxing of condensed tar." They also stated that "the yield of tar decreases and the yield of gas increases with the temperature owing to pyrolysis of the volatile products distilled from the coal." Examination of the curves in Figs. 1 and 2 shows that the yield of "ammonia and liquor" decreases above 700° C and "light oil" above 1,000° C. Obviously some pyrolysis of each of these primary products takes place, and decomposition products from them, as well as from the tar, tend to increase the yields of gas and coke as carbonization temperatures are increased.

In order to determine to what extent the decomposition of each primary product contributed to the yields of other primary products each time the carbonizing temperature was raised 100° C, Table VIII was prepared from data contained in Table VII. The left-hand portion of this table,

VIIIA, shows the increase or decrease of each primary product for each 100° rise in percent by weight of the coal. The right-hand portion of the table, VIIIB, shows the increase or decrease of each primary product in percent of the total increase or decrease of all products. For example, between 500 and 600° C, according to Table VIIIA, the decrease in coke yield amounted to 4.7 percent. All the other primary products together increased by the same amount. Their individual increases were tar 0.8 percent, liquor and ammonia 0.95 percent, light oil 0.08 percent, and gas 2.87 percent. Table VIIIB shows that coke was the only product that decreased in yield (100 percent), and its decomposition products went 17.0 percent to tar, 20.2 percent to liquor and ammonia, 1.7 percent to light oil, and 61.1 percent to gas. The following conclusions may be drawn from the data in Table VIII for the temperature intervals between 600° and 1,100° C.

600 to 700° C: Both coke and tar were decomposed in this range, coke accounting for 66.7 percent of the total, and tar 33.3

TABLE VIII

Effect of Each 100° C Rise above 500° C on Yields of Primary Products
from Pratt Coal [2]

A						B				
Increase or Decrease for Each 100° C Rise in Percent by Weight of Coal					Temperature Interval °C	Increase or Decrease for Each 100° C Rise in Percent of Total Increase or Decrease				
Coke	Tar	Liquor and Ammonia	Light Oil	Gas and Loss		Coke	Tar	Liquor and Ammonia	Light Oil	Gas and Loss
−4.7	+0.8	+0.95	+0.08	+2.87	500–600	−100.0	+17.0	+20.2	+1.7	+61.1
−2.2	−1.1	+0.44	+0.05	+2.81	600–700	−66.7	−33.3	+13.3	+1.5	+85.2
−1.0	−0.5	−0.10	+0.18	+1.42	700–800	−62.5	−31.3	−6.2	+11.2	+88.8
−0.3	−0.7	−0.23	+0.14	+1.09	800–900	−24.4	−56.9	−18.7	+11.4	+88.6
+0.3	−1.1	−1.01	+0.07	+1.74	900–1,000	+14.2	−52.1	−47.9	+3.3	+82.5
+0.7	−1.4	−1.85	−0.15	+2.70	1,000–1,100	+20.6	−41.2	−54.4	−4.4	+79.4

percent. Pyrolysis of these two materials yielded liquor and ammonia 13.3 percent, light oil 1.5 percent, and gas 85.2 percent.

700 to 800° C: In this temperature range, coke, tar, and liquor plus ammonia were decomposed, coke accounting for 62.5 percent, tar for 31.3 percent, and liquor plus ammonia for 6.2 percent of the total. The products of their pyrolysis were divided between light oil 11.2 percent and gas 88.8 percent.

800 to 900° C: Coke, tar, and liquor were decomposed, but the major change was now in tar instead of coke, the proportions being coke 24.4 percent, tar 56.9 percent, and liquor 18.7 percent. Products from them were divided between light oil, 11.4 percent, and gas, 88.6 percent.

900 to 1,000° C: Coke yield increased in this range together with light oil and gas. The proportions were 14.2, 3.3, and 82.5 percent, respectively. They were increased at the expense of tar, 52.1 percent, and liquor plus ammonia, 47.9 percent.

1,000 to 1,100° C: Only coke and gas increased in this range, coke making up 20.6 percent of the total and gas 79.4 percent. Their increases came from tar 41.2 percent, liquor plus ammonia 54.4 percent, and light oil 4.4 percent.

From the above analysis it appears that when the carbonization temperature is raised from 500 to 1,100° in 100° increments the volatile material in the 500° coke is largely decomposed below 900° C, tar starts to crack at 600° and reaches a maximum at 900°, liquor plus ammonia starts to break down at 700° and decomposes steadily thereafter, and light oil decomposes at 1,000°. The gas yield does not decrease in any range.

All, the above observations are concerned with the *yields* of tar and other primary products resulting from the carbonization of one bituminous coal (Pratt), in a single type and size of retort at temperatures of 500 to 1,100° C. Interesting conclusions concerning the *composition* of the tar produced at different temperatures in these same experiments may be drawn from additional data which are assembled in Table IX. From these data, the curves in Figs. 3 and 4 have been plotted. Figure 3 shows how the bases, acids, olefins, paraffins and naphthenes, aromatics, and pitch vary with carbonizing temperature. Figure 4 shows the composition of the tar at each carbonizing temperature from 500 to 1,100° C.

Figures 3 and 4 and Table IX indicate that the olefin content of the tar does not

TABLE IX

COMPOSITION OF TAR, PERCENT BY VOLUME, FROM PRATT COAL CARBONIZED AT TEMPERATURES OF 500 TO 1,100° C [2]

Carbonization Temperature °C	Distillate to 350° C					Pitch (Residue above 350° C)
	Bases	Acids	Olefins	Paraffins and Naphthenes	Aromatics	
500	1.4	17.1	4.3	18.9	20.0	38.3
600	1.3	16.2	4.7	14.5	20.4	42.9
700	1.6	15.3	3.8	6.2	24.2	48.9
800	1.7	9.1	3.7	2.2	26.0	57.3
900	1.8	5.4	4.1	1.4	29.1	58.2
1,000	1.5	3.4	3.9	0.9	27.9	62.4
1,100	1.1	2.3	4.7	0.8	22.8	68.3

vary materially between 500 and 1,100° C, that the tar-base content increases slightly to 900° C and then decreases slightly, that the tar acids decrease slowly between 500 and 700° and rapidly thereafter, that the
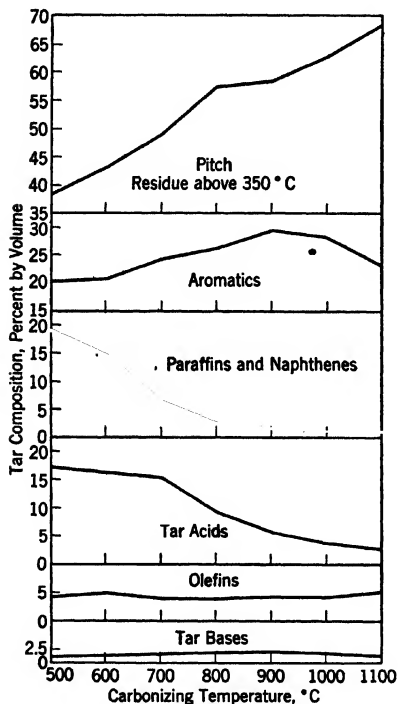
FIG. 3. Effects of carbonizing temperatures on composition of tar from Pratt coal. Concentrations of tar constituents plotted individually

paraffins and naphthenes decrease rapidly from 500 to 800° and then slowly to 1,100°, that aromatics rise to a maximum at 900°, and that pitch increases steadily throughout the entire range from 500 to 1,100° C.

According to data presented in Tables VII and VIII, pyrolysis of the tar begins at 600° C. It appears from Table VIII that between 600 and 700° C pyrolysis of

the tar can result in the formation of liquor and ammonia, light oil and gas; between 700 and 900° C in the formation of light oil and gas; between 900 and 1,000° C in the formation of light oil, gas and coke; and between 1,000 and 1,100° C in the formation of gas and coke.

In order to determine to what extent these changes take place and to study the
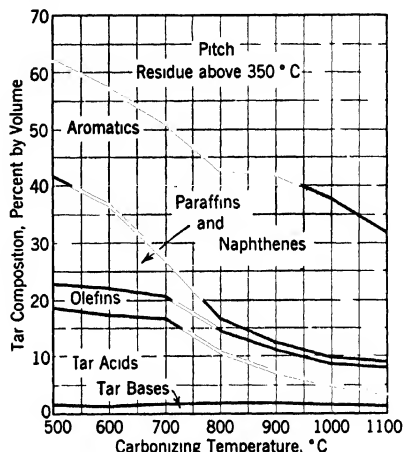
FIG. 4. Effects of carbonizing temperatures on composition of tar from Pratt coal. Concentrations of tar constituents plotted collectively.

mechanism of tar pyrolysis with resulting change in composition, Table X was prepared from data contained in Tables VII, VIII, and IX. It is based on the maximum yield of tar, which amounted to 8.4 percent by weight of the coal when carbonized at 600° C. For each 100° temperature interval it was assumed that the sum of the actual tar yield as given in Table VII and the products resulting from the pyrolysis of constituents that were present in the tar at 600° C should equal 8.4 percent. It was further assumed, as indicated by Table VIII, that the products resulting from the pyrolysis of tar constituents between 600

TABLE X

PERCENT BY WEIGHT OF 8.4 PERCENT (YIELD OF TAR AT 600° C) FOR THE TAR CONSTITUENTS AND THEIR PYROLYSIS PRODUCTS

	500°	600°	700°	800°	900°	1,000°	1,100°
Bases	1.3	1.3	1.4	1.3	1.25	0.7	0.5
Olefins	3.8	4.7	3.3	3.1	3.0	2.15	2.0
Acids	15.5	16.2	13.2	7.4	4.0	2.15	0.9
Paraffins and naphthenes	17.0	14.5	5.4	1.8	1.25	0.7	0.4
Aromatics	18.2	20.4	21.1	21.0	20.4	15.0	9.8
Pitch	34.7	42.9	42.5	46.4	42.7	38.8	29.3
Coke	9.5	....	.	..	...	3.6	11.9
Liquor and ammonia			1.4	.	. ..	....	....
Light oil	. .	....	0.2	1.0	1.7	2.1	....
Gas			11.5	18.0	25.7	34.8	45.2

and 700° were liquor and ammonia, light oil, and gas; between 700 and 900° they were light oil and gas; between 900 and 1,000°, light oil, gas, and coke; and between 1,000 and 1,100°, gas and coke. It was further assumed in these calculations that all the coke increase between 900 and 1,100° C came from the pyrolysis of constituents of tar and none of it from light oil or gas.

From the data in Table X were plotted the curves shown in Figs. 5 and 6. Figure 5 shows individually the increases and decreases of the tar components and pyrolysis products that together make up the 8.4 percent tar yield at 600° C. Figure 6 presents the same results collectively.

From the data in Table X were also calculated those appearing in Table XI. Section A gives the actual increase or decrease of each tar component and pyrolysis product in percent by weight of 8.4 percent (yield of tar at 600° C) for each 100° rise in temperature; B shows the percent of the total decrease or pyrolysis each component contributed and what percent of the total increase was contributed by each product of pyrolysis.

The following observations are based on

a study of the data presented in Tables X and XI and the curves in Figs. 5 and 6:

Between 500 and 600° C, paraffins and naphthenes (20.8 percent) and coke (79.2
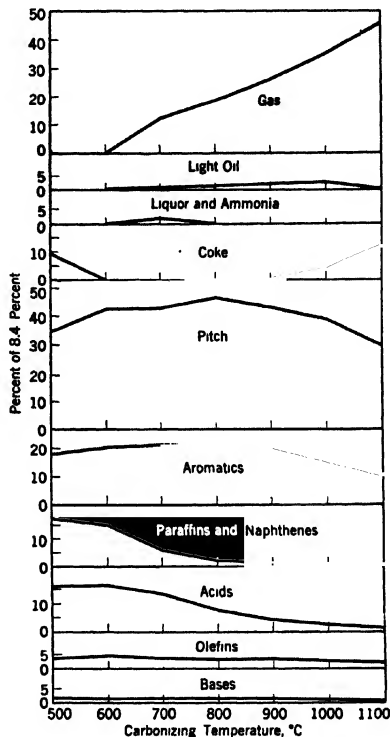
FIG. 5. Formation and pyrolysis, at different carbonizing temperatures, of the constituents of tar produced from Pratt coal at 600° C (8.4 percent). Constituents plotted individually.

percent) are decomposed with the formation of acids (5.9 percent), olefins (7.5 percent), aromatics (18.3 percent), and pitch (68.3 percent).

Between 600 and 700° C, paraffins and naphthenes (65.4 percent), acids (21.6 percent), olefins (10.1 percent), and pitch (2.9 percent) are decomposed with the forma-

tion of bases (0.7 percent), aromatics (5.0 percent), and liquor and ammonia, light oil, and gas (10.1, 1.4, and 82.7 percent respectively).

Between 700 and 800° C, paraffins and naphthenes (32.1 percent), acids (51.8 per-
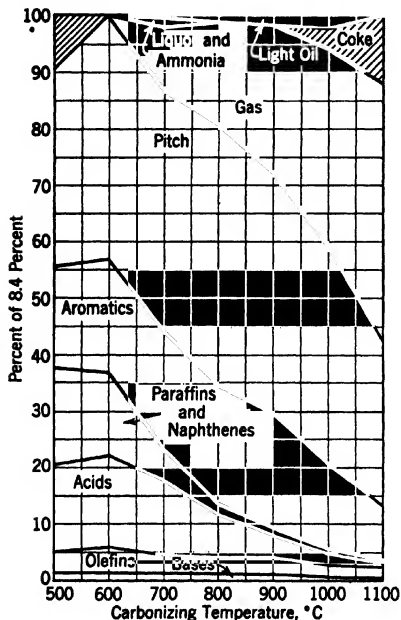
FIG. 6.   Formation and pyrolysis at different carbonizing temperatures, of the constituents of tar produced from Pratt coal at 600° C (8.4 percent).   Constituents plotted collectively.

cent), olefins (1.8 percent), bases (0.9 percent), aromatics (0.9 percent), and liquor and ammonia (12.5 percent) decompose to form pitch (34.8 percent), light oil (7.2 percent), and gas (58.0 per cent).

Between 800 and 900° C, paraffins and naphthenes (6.5 percent), acids (40.5 percent), olefins (1.2 percent), bases (0.6 percent), aromatics (7.1 percent), and pitch (44.1 percent) form light oil (8.3 percent) and gas (91.7 percent).

Between 900 and 1,000° C, paraffins and naphthenes (4.2 percent), acids (14.1 percent), olefins (6.5 percent), bases (4.2 percent), aromatics (41.2 percent), and pitch 29.8 percent) form coke (27.5 percent), light oil (3.0 percent), and gas (69.5 percent).

Between 1,000 and 1,100° C, paraffins and naphthenes (1.6 percent), acids (6.7 percent), olefins (0.8 percent), bases (1.1 percent), aromatics (27.8 percent), pitch (50.8 percent), and light oil (11.2 percent) form coke (44.4 percent) and gas (55.6 percent).

In the above analysis, it may be observed that up to 700° C aromatics are formed by the pyrolysis of some of the other tar constituents faster than they are decomposed and thereafter are decomposed faster than they are formed. It is interesting to note the yields of naphthalene salts and anthracene salts from the carbonization experiments with Pratt coal from which the other data discussed above were obtained: [11]

CARBONIZING TEMPERATURE	NAPHTHALENE SALTS	ANTHRACENE SALTS
°C	pounds per ton of coal	pounds per ton of coal
500	0	0
600	0	0
700	0	0.117
800	0.613	1.700
900	2.513	2.733
1,000	5.120	2.940
1,100	4.766	2.196

It would appear from these results that, whereas aromatics in general form between 500 and 700° C and then start to decompose at 700° C, "naphthalene and anthracene salts" form between 700 and 1,000° C and decompose between 1,000 and 1,100° C.

In general, the various observations recorded above, that are based specifically on the data furnished for Pratt coal,[2] are

11 See pp. 60 and 61 of ref. 2.

TABLE XI

EFFECT OF EACH 100° C RISE ABOVE 500° C ON YIELDS OF TAR PRODUCTS FROM PRATT COAL
(BASED ON 8.4 PERCENT TAR YIELD AT 600° C)

A

Increase or Decrease of Tar Components for Each 100° C Rise in Percent by Weight of 8.4 Percent

Temperature Interval	Paraffins and Naphthenes	Acids	Olefins	Bases	Aromatics	Pitch	Coke	Liquor and Ammonia	Light Oil	Gas
500–600	−2.5	+0.7	+0.9	0	+2.2	+8.2	−9.5	.....	.....	......
600–700	−9.1	−3.0	−1.4	+0.1	+0.7	−0.4	.....	+1.4	+0.2	+11.5
700–800	−3.6	−5.8	−0.2	−0.1	−0.1	+3.9	.....	−1.4	+0.8	+6.5
800–900	−0.55	−3.4	−0.1	−0.05	−0.6	−3.7	.....	.....	+0.7	+7.7
900–1,000	−0.55	−1.85	−0.85	−0.55	−5.4	−3.9	+3.6	.....	+0.4	+9.1
1,000–1,100	−0.3	−1.25	−0.15	−0.2	−5.2	−6.5	+8.3	.....	−2.1	+10.4

B

Increase or Decrease of Tar Components for Each 100° C Rise in Percent of Total Increase or Decrease

Temperature Interval	Paraffins and Naphthenes	Acids	Olefins	Bases	Aromatics	Pitch	Coke	Liquor and Ammonia	Light Oil	Gas
500–600	−20.8	+5.9	+7.5	0	+18.3	+68.3	−79.2	......	.....	......
600–700	−65.4	−21.6	−10.1	+0.7	+5.0	−2.9	.....	+10.1	+1.4	+82.7
700–800	−32.1	−51.8	−1.8	−0.9	−0.9	+34.8	.....	−12.5	+7.2	+58.0
800–900	−6.5	−40.5	−1.2	−0.6	−7.1	−44.1	......	......	+8.3	+91.7
900–1,000	−4.2	−14.1	−6.5	−4.2	−41.2	−29.8	+27.5	......	+3.0	+69.5
1,000–1,100	−1.6	−6.7	−0.8	−1.1	−27.8	−50.8	+44.4	... ..	−11.2	+55.6

in agreement with the following conclusions by Pryde [12] concerning the effect of temperature on tar composition and the chemical decomposition which occurs. Pryde's conclusions are based on his reviews of the published work dealing with these subjects:

There is a marked difference between the tar obtained in low-temperature carbonization and that got at higher temperatures. Low-temperature tar distilled at 450° C is brown, oily, and contains unsaturated hydrocarbons (olefins), naphthenes, paraffins, phenols, and pyridines (bases), while benzene and its homologues and solid aromatic bodies (naphthalene and anthracene salts) are absent. Tar obtained at 1,100° C is black, viscid, and contains pitch, benzene hydrocarbons, naphthalene, and anthracene, and only traces of aliphatic hydrocarbons. It is derived from low-temperature tar by progressive thermal decomposition. The thermal decomposition reactions occurring are somewhat complicated, and no attempt will be made to go into them in detail.

12 Pryde, D. R., *Gas World*, **101**, Coking Sect., 108–10 (1934).

The initial reactions include the loss of hydrogen from the naphthenes and the breaking down of the higher-boiling-point phenols and tar acids to those of lower boiling point. These reactions take place mainly between 500 and 700° C. Between 700 and 800° C the final decompositions reach a maximum. The phenols and tar acids give benzene, naphthalene, and a certain amount of carbon monoxide, ethylene, methane, and free carbon. The paraffins and unsaturated hydrocarbons give in part olefins which recondense to give aromatic hydrocarbons. The aromatic hydrocarbons, in their turn, suffer some decomposition.

Morgan and Soule [13] have presented the following conclusions concerning the effects of temperature on coal during its carbonization:

1. The decomposition of the coal substance to ordinary high-temperature tar, when subjected to the action of heat, is a process of progressive step-by-step decomposition in

13 Morgan, J. J., and Soule, R. P., *Chem. & Met. Eng.*, **26**, 1025–30 (1922).

which pyrogenetic syntheses play only a secondary part.

2. Six-membered rings and combinations thereof characterize the entire series of decomposition products from coal to high-temperature tar. The decompositions during carbonization are essentially reactions effecting the elimination of side chains.

3. The average molecular weights of the liquid intermediate products constantly decrease as the temperature of carbonization rises. This decrease is marked by the evolution of hydrogen, methane, and ethane.

4. The initial decomposition of the low-temperature tar first formed is brought about by (a) loss of hydrogen from a portion of the naphthenes with a resultant increase in the proportion of unsaturated hydrocarbons; (b) loss of side chains from the phenols by hydrogenation with the resultant formation of lower-boiling phenols; and (c) loss of hydrogen from the nitrogen bases to form a large proportion of tertiary compounds.

5. Final decompositions are at a maximum between 700 and 800° C and are marked by (a) dehydrogenation and dealkylation of the hydroaromatic unsaturated hydrocarbons and nitrogen bases to form aromatics, with the elimination of hydrogen, methane, and other simple gases; (b) hydrogenation of the phenols to aromatic hydrocarbons, and of these aromatic hydrocarbons to lower-boiling aromatics, with the formation of methane, ethane, and water; and (c) secondary, pyrogenetic syntheses of higher aromatics from simple compounds.

6. The phenols of low-temperature tar are the principal source of the monocyclic aromatic hydrocarbons. The unsaturated naphthenes of low-temperature tar are the principal source of the polycyclic aromatic hydrocarbons.

All the above considerations, which are in substantial agreement, clearly indicate that temperature of carbonization has a profound effect, not only upon the yield of tar from coal but upon the nature of the tar as well. That it has a greater effect than the type of equipment used for the carbonization and, in fact, is the governing factor will be developed in the following discussion of this phase of the subject.

EFFECT OF CARBONIZING EQUIPMENT

Coal-carbonization equipment is usually classified as low-temperature or high-temperature depending upon the temperature reached by the coke during the carbonizing process. According to Morgan,[14]

If the decomposition of the coal is carried to completion near the temperature of initial decomposition, say at 800 to 1,000° F (425 to 550° C), the process is one of low-temperature carbonization, [and] at 1,300 to 1,500° F (700 to 800° C), a second decomposition point is reached, which is characterized by the evolution of large amounts of hydrogen. If the decomposition is carried to completion at this or higher temperatures, the process is one of high-temperature carbonization and the solid residue is coke containing little or no volatile matter. · · · High-temperature carbonization as ordinarily carried on is not, however, as simple a process as the above description might lead one to believe. It is, as we shall see, a combination of low-, intermediate-, and high-temperature carbonization. The coal is not distilled at a temperature but up to a temperature. Therefore, the products of ordinary high-temperature carbonization are those of high-temperature carbonization mixed with all the substances produced by the action of heat upon the gaseous and liquid products of low- and intermediate-temperature carbonization.

Perhaps the best way to bring about a full realization of the complexity of high-temperature carbonization as outlined above is to trace the travel of heat through an unstirred charge of coal in a retort or oven.

The temperature of the walls in high-temperature carbonization varies from about 1,600° F (850 to 900° C) in a coke oven to 1,800 or 2,000° F (1,000 or 1,100° C) in a horizontal retort. This is considerably higher than is needed for complete carbonization, but is required to give the heat gradient necessary to force the heat through the charge in the short time which is characteristic of modern carbonization practice. Thus, the coal which is close to the walls of the carbonizing chamber is very rapidly heated to

14 Morgan, J. J., *Manufactured Gas*, J. J. Morgan, New York, N. Y., 1st ed., 1926, Vol 1, pp. 62–3.

the temperature of the walls. Its carbonization approaches very nearly to a true high-temperature carbonization.

On the other hand, the coal in the interior of the charge is heated very slowly, and its final temperature may be 200 to 300° F lower than the temperature of the walls. It undergoes all of the stages from low- to high-temperature carbonization. Therefore, it is very easy to see that the products of the low- and intermediate-temperature carbonization of the coal in the interior of the charge are subject to the decomposing action of heat as they escape through the hot coke and along the hot walls of the oven or retort.

The coke is a high-temperature coke in that it is almost completely freed of its volatile matter. The gas and tar, however, are mixtures of high-temperature products with the products resulting from the decomposition by heat of the low- and intermediate-temperature gases and tars.

The last statement is particularly significant. It indicates that coke, depending upon the temperature to which it is heated before leaving the carbonizing equipment and the extent to which it is freed of its volatile matter, can be classified either as low-temperature coke or high-temperature coke, regardless of the type of carbonizing equipment used. It is customary for tars produced in the making of low-temperature coke to be called low-temperature tars and for those produced in the making of high-temperature coke to be called high-temperature tars, but it does not follow that all so-called low-temperature tars have only the characteristics that are typical of true low-temperature tars. In fact, some tars produced in the making of low-temperature coke have many of the characteristics of high-temperature tars. Also, it does not follow that all so-called high-temperature tars have only the properties that characterize true high-temperature tars. Some of them have many of the characteristics of low-temperature tars as well.

Gluud and Jacobson [15] characterized low-temperature tar as follows:

1. It must be liquid at room temperature. (The liquid condition may be impaired somewhat by small paraffin deposits.)
2. Its specific gravity at 25° C (77° F) must remain between 0.95 and 1.06.
3. In thin layers it must resemble an oil varying from red-gold to port-wine in color.
4. When fresh, it smells of hydrogen sulfide or ammonium sulfide; in no case should a naphthalene odor be noticeable.

LOW-TEMPERATURE CARBONIZATION—DISCO PROCESS

No tar produced in the United States at this time on a commercial scale fully complies with the above requirements for low-temperature tar although one installation produces low-temperature coke. The process used, known as the Disco process, has been described by Denig in Chapter 21, by Lesher,[16] and by several United States Patents.[17] The coke contains about 16 percent volatile matter. Its temperature when it leaves the retort is approximately 425° C (800° F). There can be no doubt about its being true low-temperature coke; but the tar, instead of having a specific gravity at 25° C between 0.95 and 1.06, has, according to Davies,[18] a specific gravity of 1.14. Also, according to Davies, the Disco tar, in bulk, is black and "makes a greenish smear." Even when filtered to remove the coal dust and other suspended solids which it contains, thin smears of Disco tar on bright surfaces show a dark brownish red color instead of the red-gold to port-wine

15 See p. 86 of ref. 7.
16 Lesher, C. E., *Trans. Am. Inst. Mining Met. Engrs.*, **139**, 328–63 (1940); *Ind. Eng. Chem.*, **33**, 858–9 (1941).
17 Wisner, C. B., U. S Pats. 1,490,357 (1924), 1,748,815, 1,756,896 (1930), 1,835,128 (1931), 1,967,762 (1934), 1,993,198, 1,993,199 (1935). Lesher, C. E., U. S. Pat. 2,080,946 (1937).
18 Davies, C., Jr., *Ind. Eng. Chem.*, **33**, 860–4 (1941).

color prescribed for low-temperature tars. Disco tar also is viscous; true low-temperature tars are thin and oily. Preheating and partial surface oxidation of the coal, recirculation of heated breeze, vigorous stirring by the rotation of the retort, and partial combustion of vapors and gases within the retort by air admitted for the purpose are undoubtedly some of the factors that tend to produce high-temperature tar in equipment making low-temperature coke. They cause a part of the low-temperature tar, first liberated from the coal, to be decomposed, with the formation of products normally found in high-temperature tar. A tar having intermediate characteristics is produced.

HIGH-TEMPERATURE CARBONIZATION

Curran-Knowles Process. The Curran-Knowles process of coal carbonization, used in two United States plants of the Midwest-Radiant Corporation at West Frankfort and Millstadt, Ill., produces high-temperature coke of low volatile content; but the tar has many of the characteristics of low-temperature tar. It is thin and oily and contains large amounts of tar acids, which are largely of the high-boiling variety usually found in low-temperature tars. The construction and operation of the sole flue ovens used in the Curran-Knowles process are also described by Denig in Chapter 21, by Thiessen, Stevenson, Given, and Curran.[19] According to Curran:

The process is based on the use of the sole flue oven where coal is carbonized by spreading a relatively thin layer on a horizontal hearth and heating it from beneath. The fundamental coking reaction taking place under these conditions is very different from

19 Thiessen, G., *Ind. Eng. Chem*, **29**, 506–13 (1937). Stevenson, W. W., *Am. Gas J.*, **148**, No. 2, 9–13 (1938). Given, I. A., *Coal Age*, **45**, No. 5, 33–5 (1940). Curran, M. D., *Ind. Eng. Chem.*, **33**, 850–2 (1941).

that which occurs when coal is treated at the same temperatures in the vertical-slot-type coking chamber or the common gas retort. Of considerable importance is the fact that a part of the gases distilled from the coal pass up through the coal layer and preheat the coal, with the result that much faster coking speeds are developed. This reaction is also accompanied by less than the usual amount of cracking of the tarry gases with higher yields of tar and less graphitic carbon deposit on the coke substance.

The tar from Curran-Knowles ovens, like that from the Disco process, has characteristics intermediate between true low-temperature and true high-temperature tars. A part of the low-temperature tar first liberated from the coal is transformed by pyrolysis into high-temperature tar by coming in contact with highly heated coke near the hot floor of the oven or with the oven floor itself. The remainder of the low-temperature tar coming from the comparatively cool middle and top portions of the coal layer is not decomposed, at least not to the same extent as that from the bottom of the charge. The mixed tars resulting from these operations closely resemble that from the Disco process. In other words, two carbonizing processes, one of which makes low-temperature coke and the other high-temperature coke, produce tars having similar characteristics.

Vertical Retorts. Vertical retorts, both intermittent and continuous, are generally considered to represent one type of high-temperature carbonizing equipment. The coke is heated to high temperatures and is substantially devolatilized before it is discharged. However, like Curran-Knowles ovens and for much the same reason, vertical retorts produce tars that have some of the characteristics of low-temperature tars.

The construction and operation of vertical retorts are discussed by Denig in Chapter 21, by Porter,[9] Morgan,[14] and others.

Morgan [20] has made the following statement concerning the tar from vertical retorts:

Tar and ammonia yields are higher and the tar is less degraded. There is less lamp black, cyanogen, and naphthalene formed. This is doubtless due to the smaller area and cone shape of the carbonizing layer in the continuous vertical. The result is that much of the gas and vapors pass up through the cool coke in the center of the retort and are not subjected to the decomposing effect of the hot coke and hot retort walls. Naphthalene troubles are practically unknown in continuous vertical systems, and the tar is very low in pitch.

As the coal passes downward in continuous vertical retorts, it passes slowly through constantly increasing zones of temperature. Low-temperature tar liberated in the upper and cooler part of the retort may escape with little decomposition. Some of the tar produced further down may come in contact with moderately or highly heated walls, but much of it undoubtedly escapes through the coal with little decomposition. The combined tar which emerges from the retort therefore contains tars which have been subjected largely to low-temperature conditions, to some extent to mid-temperature conditions, and only to a small extent to high-temperature conditions. Its characteristics are intermediate between those of low- and high-temperature tars.

Byproduct Coke Ovens. Horizontal-chamber, slot-type, byproduct coke ovens, as normally constructed and operated in the United States, produce high-temperature coal tars. Their development, construction, and operation have been discussed at length by Denig in Chapter 21. Temperature conditions and the course of gas travel in the charge in byproduct coke ovens have been discussed by Porter: [21]

20 See p. 128 of ref. 14.
21 See p. 148 of ref. 9.

The gaseous products do not pass entirely along the hot walls of the oven, nor do they find exit in any considerable amount through the uncoked center of the coal charge. The main portion passes through the coked and partly coked region in the charge, backward, toward the walls, from the advancing ring or shell of fused coal. It seeks the easiest passage—where the material is relatively porous and in some measure fissures have developed. Naturally, in paths of least resistance, much of these products seeks its egress along the open space where, near the wall especially, the hardened coke has drawn away a little to leave openings. But the principal portion passes upward and out of the charge through the coking mass without reaching the hot walls.

Much decomposition of the primary tars and gases, arising from the pasty fused layer of coal, takes place as these products pass through the heated zones. Carbon is deposited thereby on the coking material, not loosely as soot, but in a hard, cementing form which aids in strengthening the coke.

A small amount of gas and vapors, containing a large proportion of steam, must pass out through the inner core of uncoked coal. It comprises essentially the initial carbonization products, formed from the coal while being heated to the fusion or pasty stage, i.e., up to 350° C. This is relatively a very small part of the total gaseous products, and it undergoes little or no secondary decomposition until it reaches the hot open space above the charge.

In byproduct coke ovens substantially all the tar, before it leaves the ovens, is heated sufficiently to decompose the paraffins, naphthenes, and high-boiling tar acids originally present in the primary tar first liberated from the coal and to form in the tar substantial amounts of naphthalene, anthracene, and other hydrocarbons and pitch. True high-temperature tar closely approximating that produced at 900 to 1,100° C in the experimental retorts used in the BM-AGA tests [2] is produced. If the tar leaving the coal charge is heated too long or too high in the free space above the charge, decomposition of some of the tar

constituents occurs with the formation of coke and gas. The resulting tar then resembles, to some extent, the tar produced in horizontal retorts.

Horizontal Retorts. The tar from horizontal retorts is high-temperature tar that has been cracked to a considerable extent by prolonged contact with highly heated walls and coke. Horizontal retorts are heated uniformly to a high temperature (about 1,000 to 1,100° C) throughout their entire length. Tar escaping from coal particles in any part of the retort can hardly fail to come in contact with hot walls before leaving the retort. The tar, first liberated from the coal as primary or low-temperature tar, passes successively through mid- and high-temperature stages and then a large proportion of it is further altered or decomposed by contact with the highly heated retort walls. Some of the constituents, first formed under mid- and high-temperature conditions, are cracked with the formation of gas and coke, and the physical and chemical characteristics of the high-temperature tar are altered appreciably. Viscosities, specific gravities, free carbon, and pitch contents are increased, and distillate yields are decreased.

Actually, the walls of most horizontal retorts are not heated much hotter than those of byproduct coke ovens, but the ratio of wall surface to coal charge is greater in horizontal retorts, and the space above the coal charge through which the tar must pass has the same high temperature as the remainder of the retort. These conditions cause a greater proportion of the tar to be decomposed. The effect of such decomposition is shown in Fig. 7, the curves for which were plotted from the analyses of forty-five typical high-temperature coal tars. Three of them came from vertical retorts, thirty-three from byproduct coke ovens, and nine from horizontal retorts.

In the specific gravity range of 1.09 to 1.215, which is the range for vertical-retort and byproduct coke-oven tars in Fig. 7, the various curves are continuous, indicating that naphthalene content, tar acids, percent distillate to 300° C, percent distillate to 355° C, and benzol-soluble material change in regular order with increasing specific gravity. But the curves break at 1.22 specific gravity, which is the start of the range for the horizontal-retort tars. Apparently some condition other than temperature accounts for the fact that the horizontal-retort curves are not merely continuations of those for the vertical and byproduct coke-oven tars. The explanation appears to lie in the fact, mentioned above, that in horizontal retorts a greater proportion of the tar comes in contact with highly heated retort walls and more of it is thermally decomposed than in coke ovens even though the side walls of the ovens may be heated to approximately the same temperatures as the walls of the horizontal retorts.

This hypothesis is supported by analytical data for one hundred and fifty tars produced from different coals in a single experimental retort,[2] the same retort that was used for the tests on Pratt coal which were discussed earlier in this chapter. Volkmann [22] plotted the specific gravities of the tars produced in these tests against carbonization temperatures. On the right-hand side of Fig. 7 are given the ranges of specific gravity and also the average specific gravity for each 100° rise in temperature as plotted by Volkmann. At 1,100° C the average specific gravity was 1.20. At 1,200° C (extrapolated) it was 1.225. According to Fieldner,[23] this is the

22 Volkmann, E. W., dissertation, Columbia University, 1935, p. 69.
23 Fieldner, A. C., *U. S. Bur. Mines, Tech. Paper* **396** (1926), 46 pp.

maximum temperature in high-temperature carbonization, and yet all the specific gravities for horizontal-retort tars in Fig. 7 are higher than 1.225. Prolonged contact of the tar or contact of a greater proportion of it with walls heated to 1,100 to 1,200° C

But, in high-temperature carbonization, the shape, the size, the method of heating, the amount, and the temperature of the space above the coal charge, and other factors, tend to influence the extent to which the primary tar, first produced by thermal de-
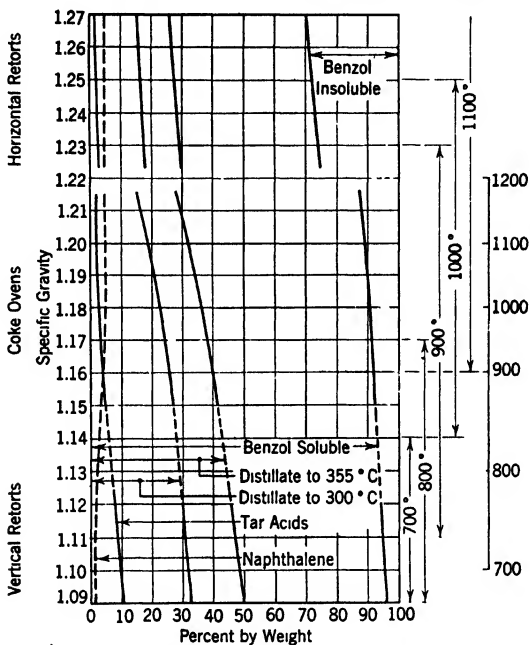
FIG. 7. Relationships between the specific gravities and compositions of forty-five typical coal tars from vertical retorts, coke ovens, and horizontal retorts.

could account for the higher specific-gravity range and for the large amount of decomposition indicated by the high percentage of benzol-insoluble material in the horizontal-retort tars.

<center>GENERAL</center>

In general it may be concluded that the major factor that influences the characteristics of the tar produced in different types of carbonizing equipment is temperature.

composition of the coal, is itself decomposed. Vertical retorts, Curran-Knowles ovens, and Disco-process retorts all produce tars that contain substantial amounts of low-temperature mixed with high-temperature tar. Their specific gravities lie in the range of 1.09 to 1.14. Byproduct coke-oven tars which range in specific gravity from 1.145 to 1.22 contain some low-temperature tar in the lower part of the range, but little or none as the specific gravity

rises to 1.22. At this point all the tar probably is of the high-temperature variety, all the low- and mid-temperature tars having been converted into this type by pyrolysis. Horizontal-retort tars have specific gravities above 1.22 because the high-temperature tars formed in them by the pyrolysis of primary tars are further decomposed with the formation of coke and gas.

Including true low-temperature tar as one type, it will be seen from the above that there are four types of coal tar which may be divided according to specific-gravity ranges approximately as follows:

	SPECIFIC GRAVITY (at 15.5° C)
1. True low-temperature tar	0.98 to 1.09
2 Low-temperature tar containing an increasing proportion of high-temperature tar	1.09 to 1.14
3 High-temperature tar containing a diminishing proportion of low-temperature tar	1.14 to 1.22
4 High-temperature tar partially decomposed by pyrolysis	1.22 to 1.27

ANALYSES OF COAL TARS PRODUCED IN THE UNITED STATES

The effects of coal, carbonizing temperature, and type of carbonizing equipment on the physical and chemical characteristics of coal tars have been discussed in preceding pages. Reasons for differences in the nature and compositions of coal tars produced in low-temperature, rotary retorts, sole-flue heated ovens, vertical retorts, by-product coke ovens, and horizontal retorts have been given. In Table XII are presented typical analyses of tars produced by these five types of equipment in the United States. The methods of analysis used in obtaining the data for Table XII, reasons for their selection, and the significance of the analytical results are as follows:

Specific Gravity. (Hydrometer method, A.S.T.M. Standard D70-27.[24]) In general, the specific gravities of coal tars rise with increasing temperatures of carbonization regardless of the types of coal or carbonizing equipment used. This is borne out by the specific gravities of the vertical-retort, coke-oven, and horizontal-retort tars in Table XII. But it is not indicated by the specific gravities of the low-temperature, rotary-retort, or the sole-flue-oven tars. The presence of coal dust, coke dust, and lampblack resulting from partial combustion of gas and volatile materials in the retorts by air admitted for the purpose, undoubtedly is responsible for the abnormally high specific gravity of the rotary retort tar; on the basis of carbonizing temperature alone it should have a lower specific gravity than any of the other tars represented in the table.

The sole-flue-oven tar, as previously pointed out, contains tars that have been subjected both to low-temperature and high-temperature conditions. In the analysis given in Table XII, its specific gravity is slightly higher than that of the vertical-retort tar, indicating a higher content of high-temperature tar, although its tar acid content and distillation-test results indicate a higher content of low-temperature tar.

Absolute Viscosity. (Koppers Capillary Rise Viscometer [25]) This method of viscosity measurement was selected in order that the viscosities of all the tars might be measured at a single temperature, for purposes of comparison. In Table XII are given the absolute viscosities in centistokes at 35° C for all the tars and at 20 and 50° C for some of them. The influence of the solid material contained in the rotary-retort tar is again evidenced by its comparatively high viscosities at 20 and 35° C. The viscosities of the other tars increase in the expected manner and in the order of the carbonizing temperatures to which they were subjected during their formation.

Temperature Susceptibility Factor. Calculated by means of the following formula de-

24 *A.S T.M. Standards*, Pt. II, American Society for Testing Materials, Philadelphia, 1942, p. 496.

25 Rhodes, E. O., Volkmann, E. W., and Barker, C. T., *Eng. News-Record*, 115, 713–7 (1935).

TABLE XII

ANALYSES OF TYPICAL TARS

Type of Carbonizing Equipment	Rotary Retort (Disco Process)	Sole-Flue Oven (Curran-Knowles)	Vertical Retort	Byproduct, Coke Oven (Koppers) Average	Heavy	Horizontal Retort
Specific gravity at 15.5/15.5° C	1.141	1.113	1.103	1.180	1.226	1.249
Absolute viscosity, centistokes						
at 20° C	3,545	253	1,493	1,931	......	......
at 35° C	530	63	237	316	2,850	14,090
at 50° C	.....	.....	.....	.....	493	2,065
Viscosity temperature susceptibility, S	1.19	1.28	1.29	1.21	1.16	1.04
Carbon I (nitrobenzene-insoluble)	12.3	2.1	2.2	2.5	10.8	17.3
Carbon II (acetone-insoluble, tar-soluble)	0.2	1.1	2.6	8.7	10.8	12.3
Benzene-insoluble	13.6	3.4	3.5	4.6	12.0	21.0
Distillation, percent by weight						
to 170° C	1.8 ...	2.1	1.2	0.7	0.4	1.5 ....
to 200° C	3.3 . .	4.3	2.6	1.1	0.7	1.7 . .
to 210° C	5.0 ...	7.4	4.0	1.8	1.3	2.0 ....
to 235° C	13.2 . ..	22.3	11.4 . .	7.1 ...	6.1	4.3 ....
to 270° C	25.8 . ..	33.8 .	21.2 ..	18.2 . .	15.4 . .	11.0 ....
to 300° C	35.4 33.9	41.8 41.7	28.8 28.2	26.3 24.9	20.9 20.1	17.5 15.2
to 315° C	... 39.2	... 45.6	. 32.7	. 28.3	. . 21.8	.... 17.6
to 335° C	... 44.2	. 53.8	. . 40.6	.... 33.4	... 25.8	.... 21.0
to 355° C	55.8	. 61.6	... 49.6	... 41.9	... 34.0	.... 30.3
Residue	62.4 42.4	57.6 37.7	70.8 49.7	73.7 57.6	78.2 65.9	82.3 69.6
Softening point of distillation residue (R.B.)						
residue at 270° C	77.5° C	37.2° C	30.9° C	41.5° C	41.6° C	56.0° C
residue at 300° C	93.5°	45.5°	37.2°	48.5°	53.0°	59.2°
residue at 355° C	209.0°	94.2°	80.0°	89.8°	80.4°	108.5°
Tar acids in 0-270° fraction, percent by volume of tar	17.5	18.4	7.36	2.01	2.2	1.21
Naphthalene in 170-235° fraction, percent by volume of tar	Trace	Trace	0.55	7.45	6.3	5.31
Sulfonation factors						
0-300° C fraction	1.27	1.79	3.11	....	0.04	0.42
300-355° C fraction	....	Trace	1.86	....	0.03	0.14

veloped by Nevitt and Krehma [26] for the determination of the susceptibility (S) of viscosity to temperature changes:

$$ S = 0.221 \times \frac{\log \left(\dfrac{\log V_1 + 0.08}{\log V_2 + 0.08} \right)}{\log \dfrac{T_2}{T_1}} $$

where V_1 and V_2 are absolute viscosities measured at absolute temperatures T_1 and T_2 respectively. Coal tars are highly complex systems in which solids of microscopic and ultramicroscopic size are suspended in an oily medium. Change in viscosity with temperature, at least in part, is a function of

[26] Nevitt, H. G., and Krehma, L. C., *Ind. Eng. Chem., Anal. Ed.*, **9**, 119–22 (1937).

the number and degree of dispersion of the suspended particles in the tar; the finer and more numerous the suspended particles, the smaller the change in viscosity with change in temperature.

Comparison of the susceptibility factors in Table XII, except that of the rotary-retort tar, indicates that the susceptibility of viscosity to temperature change decreases in coal tars as carbonizing temperatures increase. The fact that the rotary-retort tar, produced at the lowest carbonizing temperature, has a susceptibility factor in the range of the coke-oven tars, is probably due to the coal which it contains, a part of the coal being dispersed in the oily medium of the tar in such a fine state of subdivision as to influence its temperature susceptibility. Similar dispersoids, prepared from coal and tar,

have been described by Evans and Pickard [27] and others.

Carbon I (Tar-Insoluble Material). A sample of the tar to be tested, of such size that the final quantity of tar-insoluble material is about 0.1 gram, is dissolved in high-boiling coal tar oil (whose insoluble content has been determined) or nitrobenzene by heating to 70° C with stirring. The solution is filtered with suction through a filtering crucible containing 1.0 gram of a dried filter-aid. When filtration is complete, two successive portions of creosote at 70° C are poured through the filter from the beaker in which the tar was first dissolved to wash adhering particles from the beaker and to wash the undissolved portion of the tar contained in the crucible. Washing is then continued with nitrobenzene in 5- to 10-milliliter portions, stirring the filter mat at intervals, until the filtrate is clear. After washing with 5- to 10-milliliter portions of acetone or benzene to remove the nitrobenzene, the crucible is dried at 105° C for 30 minutes, cooled in a desiccator, and weighed. The increase in weight of the crucible, minus the amount of insoluble material from the creosote used, divided by the weight of tar tested, gives the percentage of tar-insoluble material or Carbon I.

This method of test is based upon the researches of Hodurek,[28] who found that the amount of material dispersed in tar that is insoluble in the tar itself (which he called Carbon I) may be determined directly by means of anthracene oil in a manner similar to the above. The amount of tar-insoluble matter determined in this manner compares favorably with the amount which may be removed from the tar directly by filtration. According to Mallison,[29] "This coarse free carbon, which can be isolated by filtration of the nitrobenzene solution, can be considered as a kind of filler, which gives a certain stability to the system. The finely dispersed, so-called free carbon, the particle size of which varies from microscopic to ultramicro-

scopic, determines the adhesive and binding properties of the tar."

The high Carbon I content of the rotary-retort tar is a measure of the coal and lampblack particles of microscopic size contained in it, for, without such contamination, tar produced at the low temperature employed in this process could be expected to have even less Carbon I than the sole-flue-oven or vertical-retort tars. The higher Carbon I contents of the coke-oven and horizontal-retort tars reflect the higher temperatures at which they are produced, insoluble carbon particles being formed by the pyrogenetic decomposition of high-molecular-weight hydrocarbons contained in the oily medium, which also are produced by elevated temperatures of carbonization.

Carbon II (Acetone-Insoluble Tar-Soluble Material). To a sample of the tar to be tested, of sufficient size to yield about 0.1 gram of acetone-insoluble material, is added 0.5 milliliter of nitrobenzene. The beaker containing the tar and nitrobenzene is warmed gently, shaken until the tar has dissolved in the nitrobenzene, distributed evenly over the bottom and 2 centimeters up the sides of the beaker, and cooled to room temperature, and 100 milliliters of acetone is added. The first 10 milliliters of acetone is added slowly and with constant shaking to distribute the precipitate evenly over the bottom and sides of the beaker. The remainder of the acetone can be added more quickly. After being stirred mechanically for 30 minutes at room temperature, the solution is filtered through a Royal Berlin A-2, 13502 filtering crucible. Washing is done with the filtered acetone solution made up to 100 milliliters with fresh acetone followed by a final wash with not more than 10 milliliters of fresh acetone, using suction on the crucible. After drying for 20 minutes, the crucible is cooled in a desiccator and weighed. The weight of the precipitate divided by the weight of sample taken gives the percentage of acetone-insoluble material in the tar. The Carbon II content of the tar is calculated by subtracting the Carbon I content, determined as described above, from the percentage of acetone-insoluble material. The difference, or Carbon II content, represents that portion of the tar which is soluble in the tar itself but insoluble in acetone.

This test, like the Carbon I determination

[27] Evans, E. V., and Pickard, H., *An Investigation Into the Nature and Properties of Coal Tar,* South Metropolitan Gas Company, London, 1931, p. 28.

[28] Hodurek, R., *Mitt. Inst. Kohlenvergasung,* 1, 9–10, 19–21, 28–30 (1919).

[29] Mallison, H., *Proc. 3rd Intern. Conf. Bituminous Coal,* 1, 947–57 (1931).

described above, is based upon the work of Hodurek except that acetone is used instead of benzene. Acetone gives a greater differentiation between different tars than carbon disulfide or benzene and is a more satisfactory test material than ethyl ether or petroleum ether.[30]

Volkmann, Rhodes, and Work [30] have stated "that the percentage of binding constituents in coal tars may perhaps be evaluated or indicated by the amount of C-II as determined by acetone extraction." This has been confirmed by comparing the Carbon II contents of tars and pitches with their binding capacities as determined by laboratory and service methods.

The direct relationship between Carbon II content and conditions of carbonization is shown by the Carbon II results reported in Table XII. Figure 8 shows the rise in Carbon I and Carbon II content with rise in specific gravity for the vertical-retort tar, coke-oven tars, and horizontal-retort tars whose analyses are given in Table XII. The curves indicate that a steady increase in the Carbon II content takes place as the specific gravity increases, probably because resinous constituents of high molecular weight are formed by polymerization as the temperature of carbonization and amount of contact between tar and heated surfaces are increased. The curve for Carbon I shows that, with lower temperatures and less contact with heated surfaces which give high-temperature tars of comparatively low specific gravity (below 1.18), little decomposition of the tar occurs but a large and increasing amount of decomposition takes place as the specific gravities increase owing to more severe carbonizing conditions.

Benzene-Insoluble Matter: A 3- to 10-gram sample of tar (depending upon the estimated insoluble material) is digested for 20 to 30 minutes with 60 milliliters of toluene at 90 to 100° C. The toluene-tar mixture is decanted into a weighed Alundum thimble, washed with pure benzene, and allowed to drain. It is then extracted with hot refluxed benzene until the benzene leaving the Alundum thimble is colorless. The thimble is then dried at 97 to 100° C, cooled in a desiccator, and weighed. The increase in weight

30 Volkmann, E. W., Rhodes, E. O., and Work, L. T., *Ind. Eng. Chem.*, **28**, 721–34 (1936).

divided by the weight of sample tested represents the percentage of benzene-insoluble material which the tar contains.

Test results by this method represent Carbon I plus Carbon II as determined by Hodurek,[28] the Carbon II in this case being benzene-insoluble tar-soluble material instead of the acetone-insoluble tar-soluble material previously discussed.
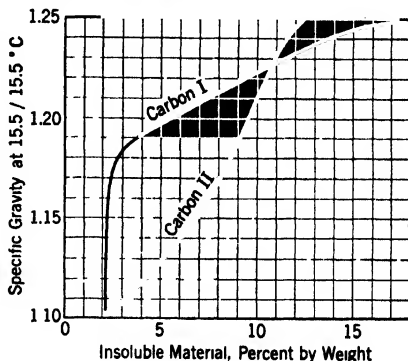
Fig. 8.   Relationships between insoluble-material contents and specific gravities of the vertical retort tar, coke-oven tars, and horizontal-retort tars whose analyses are given in Table XII.

The benzene-insoluble data in Table XII have the same significance as the sums of the Carbon I and Carbon II results reported there, but the greater differentiations due to the use of acetone as mentioned above are apparent. Also, the benzene-insoluble results alone have little significance as compared with separate Carbon I and Carbon II determinations.

Distillation. (A.S.T.M. Standard Method D20-30.[31]) With the exception of the rotary-retort tar, the distillation results in Table XII show the gradual decrease in the amount of distillate to each temperature with increasing carbonizing temperatures. The slightly increased amounts of distillate to 170, 200, and 210° C in the horizontal-retort tar indicates that the excessive decomposition which takes place in horizontal retorts forms low-boiling oils as well as Carbon I and Carbon II. Obviously, high-molecular-weight

and high-boiling compounds break down with the formation of carbon and some low-molecular-weight compounds. The diluting effect of the Carbon I in the horizontal-retort tar is seen by the fact that its percentages of distillate to different temperatures are lower than those of the Curran-Knowles tar.

Softening Points of Distillation Residue. (Ring and Ball Method A.S.T.M. D36-26.[32]) In general the softening points of the distillation residues at 270, 300, and 355° C increase with increasing carbonizing temperatures as shown by the vertical-retort, coke-oven, and horizontal-retort tars. This is probably caused by the increase in Carbon I, which concentrates in the distillation residue, and by the fact that distillation of the tars containing higher percentages of Carbon II causes some decomposition of Carbon II into Carbon I, as pointed out by Hodurek, the Carbon I formed in this manner further increasing the residue softening points.

The fact that the residue softening points of the rotary-retort tar are higher than those of the horizontal-retort tar may be due to the increased amount of solution or dispersion of the coal contained in this tar which takes place as its temperature increases during distillation.

Tar Acids and Naphthalene. Sixteen hundred grams of tar is distilled to 270° C vapor temperature. The distillate to 270° C is extracted three times with a 15 percent sodium hydroxide solution. The phenolate is sprung with 40 percent caustic soda solution and poured through a known volume of xylene. The increase in volume of the xylene is the volume of dry tar acids extracted from the tar oil. This volume, divided by the original volume of the tar, gives the percentage of tar acids by volume obtainable from the tar by distillation to 270° C.

The neutral oil remaining after the extraction of tar acids is redistilled, and the fraction from 170 to 235° C is cooled to 25° C for at least 2 hours, and preferably overnight. The oil is then pressed in a 2.25-inch cylinder with a total pressure of 8 tons. The dry cake is adjusted, if necessary, to the desired softening point by the admixture of some of the filtrate from the pressing operation. Its weight is determined and volume calculated.

The tar acid and naphthalene results in

32 See p. 488 of ref. 24.

Table XII clearly show the effect of carbonizing temperature and carbonizing conditions on the chemical composition of the tar. The decomposition of tar acids and formation of naphthalene with increasing carbonizing temperatures are evident.

Sulfonation Factor. (A.A.S.H.O. Standard Method T108-42.[33])

The comparatively high sulfonation factors of the rotary-retort, sole-flue-oven, and vertical-retort tars confirm the statements previously made that tars produced at lower temperatures contain higher proportions of paraffins and naphthenes. The fact that they are decomposed at higher temperatures is shown by the low sulfonation factors of the coke-oven and horizontal-retort tars.

In the paragraphs above, the method and significance of each test as applied to the different tar samples have been discussed. In the following paragraphs the significance of the entire analysis of each tar is summarized.

Low-Temperature, Rotary-Retort Tar (Disco Process). The fact that this tar contains a large proportion of primary tar is indicated by its high tar acid content, by the absence of naphthalene in the 170 to 235° neutral oil fraction at atmospheric temperature, and by the moderately high sulfonation factor for the 0 to 300° fraction. Its specific gravity, absolute viscosities, and softening points of distillation residues are abnormally high for low-temperature tar owing to the presence of a large amount of insoluble, suspended, solid material which probably consists largely, if not entirely, of coal dust, coke dust, and lampblack. The coal dust and coke dust are entrained in the gases leaving the rotary retort, and the lampblack results from partial combustion of the gas and volatile materials which it contains by air admitted into the retorts. The amount of insoluble, suspended material present in the tar is shown by the Carbon I determination. The fact that this tar has a lower temperature susceptibility factor than either the sole-flue-oven tar or the vertical-

retort tar and is comparable in this respect to coke-oven tar probably is due to the presence of dispersed, colloidal particles of coal or lampblack. The absence of Carbon II (acetone-insoluble tar-soluble matter) shows that this tar does not contain polymerized, resinous constituents like those contained in the tars produced at higher temperatures. In general, it appears to be a low-temperature tar with a large amount of solid, insoluble matter in suspension.

Sole-Flue-Oven Tar (Curran-Knowles Process). This tar also contains a large proportion of primary tar as shown by its high tar acid content, the absence of naphthalene at atmospheric temperature in the 170 to 235° neutral oil fraction, moderately high sulfonation factor, low absolute viscosities at 20 and 35° C, and large amounts of distillate to 300 and to 355° C. That it contains some high-temperature tar as well is indicated by its specific gravity, which is slightly higher than that of the vertical-retort tar, and by the softening points of its distillation residues, which are similar to those of the coke-oven tars. Also, in susceptibility factor, Carbon I, and benzene-insoluble contents, it closely resembles the vertical-retort tar.

Vertical-Retort Tar. That the vertical-retort tar sample represented by the analysis in Table XII contained more high-temperature tar than either the sole-flue-oven or the rotary-retort tar is evidenced by the increased amount of Carbon II, the presence of naphthalene in the 170 to 235° neutral oil fraction, lower tar acid content, and smaller amounts of distillate to 300 and to 355° C. However, the presence of a considerable amount of primary tar is shown by the low specific gravity of the sample and the high sulfonation factors for the 0 to 300° and 300 to 355° fractions, the viscosities at 20 and 35° C, and, also, the softening points of distillation residues, which are lower than those of the high-temperature tars from coke ovens or horizontal retorts.

Byproduct Coke-Oven Tars. The analyses of two typical coke-oven tars are given in Table XII; one is intended to represent coke-oven tars of medium specific gravity, and the other, coke-oven tars of high specific gravity. The low sulfonation factors for the high-gravity coke-oven tar, the high naphthalene and Carbon II contents, and the higher viscosities, lower susceptibility factors, and

lower percentages of distillate to 300 and to 355° C for both samples are characteristic of high-temperature tars containing little if any primary tar.

Horizontal-Retort Tar. Previously it has been indicated that horizontal-retort tars are high-temperature tars which have been partially cracked or decomposed by the conditions of temperature and contact with highly heated surfaces to which they are exposed in the horizontal retorts. This is indicated by the analysis of a typical horizontal-retort tar given in Table XII. Its high specific gravity, high viscosities at 35 and 50° C, high nitrobenzene- and benzene-insoluble contents, high softening points of distillation residues, and low susceptibility factor all indicate that some of the constituents of the high-temperature tar first formed in the retorts have been partially decomposed.

PRODUCTION AND USE OF COAL TAR IN THE UNITED STATES

With the exception of small amounts of tar produced in gas ovens, the only tars from bituminous coal that are produced commercially in the United States are those discussed above, namely, byproduct coke-oven tar, vertical-retort tar, horizontal-retort tar, sole-flue-oven tar (Curran-Knowles process), and low-temperature, rotary-retort tar (Disco process). The quantity of each variety produced in 1942 is shown in Table XIII, from which it is clear that byproduct coke-oven tar has almost entirely displaced all other types of coal tar in the United States, for reasons explained by Denig in Chapter 21 as determining the predominant position achieved by the horizontal chamber, byproduct coke oven in the American coke industry.

Some experiments are being conducted with the Hayes process, low-temperature retorts which have been described and discussed by Woody; [34] but no commercial quantity of tar is produced by this method.

[34] Woody, G. V., *Ind. Eng. Chem.*, **33**, 841–44 (1941).

TABLE XIII

PRODUCTION OF COAL TAR IN THE UNITED
STATES IN 1942

Type of Tar	Gallons	Percent of Total
Byproduct coke-oven (horizontal-chamber) [35]	740,175,619	96.76
Vertical-retort (intermittent and continuous) [35]	13,440,106	1.75
Horizontal-retort (stop end and through) [35]	7,366,756	0.96
Sole-flue-oven (Curran-Knowles process) [35]	2,160,000	0.28
Rotary-retort (Disco process) [16]	1,500,000	0.19
Gas-oven [35]	284,967	0.04
Total	764,927,448	100.00

One low-temperature installation at Dickenson, N. D., carbonizes lignite occasionally in retorts of the Lurgi type. According to Fieldner,[36] it has a capacity of 60,000 to 70,000 tons of lignite briquets per year; and the production of tar ranges from 8 to 10 gallons per ton of briquets. The Lurgi process employed in this plant has been illustrated and described briefly by Fieldner.[28] The tar from this source is not included in Table XIII, but, if it were included, it would not appreciably affect the total quantity or the percentage of the total tar which the byproduct coke-oven tar represents—about 97 percent.

In Table XIV are presented the figures for the production and distribution of byproduct coke-oven tar in the United States in 1940, 1941, and 1942, as given in the *Minerals Yearbook* and other reports of the U. S. Bureau of Mines for those years and in the U. S. Tariff Commission Re-

ports for 1940. Of these three years, 1940 was the most nearly normal. The influence of war activities on the amount of tar produced, burned, and refined is apparent in the figures for 1941 and 1942. The table does not include the distribution of the tar from the sources mentioned above other than byproduct coke ovens, i.e., vertical retorts, horizontal retorts, sole-flue ovens, rotary retorts, and gas ovens. However, it may be assumed that the quantity of tar from these sources was about the same in 1940 and 1941 as it was in 1942, for which production figures were given above, and it may also be assumed that substantially all the tar from these sources was refined. Little or none of it was burned.

Figure 9 illustrates how the products of coal carbonized in byproduct coke ovens in the United States in 1940 were distributed. The major industries which employ products of coal carbonization and some of the products which they use are indicated.

TAR RECOVERY AT COKE PLANTS

In the byproduct-recovery system of a modern coal-carbonization plant, coal tar is removed first from the gas by combined atmospheric and direct or indirect water cooling, and light oil is removed last by scrubbing the gas with high-boiling petroleum or creosote solvents. In other words, the coal tar is removed from the gas immediately after it leaves the coke ovens, whereas light oil is recovered just before the gas enters the holder. Between these two points it is customary to remove ammonia from the gas as ammonium sulfate by bubbling the gas through sulfuric acid. Also, between the points of tar recovery and light-oil removal, phenols, pyridine bases, and naphthalene may be recovered by suitable methods if desired. The order in which these processes are or may be carried out is illustrated by Fig. 10.

[35] U. S. Bur. Mines, *Mineral Market Report* 1057 (1943), p. 2.

[36] Fieldner, A. C., *Minerals Yearbook*, U. S. Bureau of Mines, Washington, D. C., 1937, p. 949.

TABLE XIV

PRODUCTION AND DISTRIBUTION OF BYPRODUCT COKE-OVEN COAL TAR IN THE UNITED STATES*

Production	1940 Gallons	Percent	1941 Gallons	Percent	1942 Gallons	Percent
1. Coke-oven tar produced at coke plants	627,585,932	93.2	658,263,692	94.9		
2. Coke-oven tar produced at gasworks	45,700,585	6.8	45,885,776	5.1		
3 Total coke-oven tar produced	673,286,517	100.0	704,149,468	100.0	740,175,619	100.0
Uses—individual						
4. Sold for refining	311,048,511	45.8	377,790,519	52.7	443,007,596	60.1
5. Refined at coke plants	151,545,371	22.3	184,197,206	25.7	194,692,227	26.4
6 Sold for fuel to others	38,560,942	5.7	14,545,466	2.0	2,194,245	0.3
7 Sold for fuel to associates	1,081,657	0.2	203,808	0.03	395,450	0.05
8 Used by producer for fuel under boilers	3,215,363	0.5	3,225,550	0.4	1,177,945	0.15
9 Used by producer for fuel in open hearths	172,738,403	25.4	136,090,580	19.0	94,387,192	12.8
10. Used by producer for fuel otherwise	1,408,990	0.2	1,401,067	0.2	1,670,873	0.2
11. Total coke-oven tar used	679,599,237	100.0	717,454,196	100.0	737,525,528	100.0
12. Gallons to or from stock	−6,312,720	.....	−13,304,728	.....	+2,650,091	.....

	Uses, total	1940 Gallons	Percent	1941 Gallons	Percent	1942 Gallons	Percent
4 + 5	Total refined	462,593,882	68.1	561,987,725	78.4	637,699,825	86.6
6 + 7 + 8 + 9 + 10	Total used for fuel	217,005,355	31.9	155,466,471	21.6	99,825,705	13.4
4 + 6 + 7	Total sold	350,691,110	51.6	392,539,793	54.7	445,597,291	60.6
5 + 8 + 9 + 10	Total used by producer	328,908,127	48.4	324,914,403	45.3	291,928,237	39.4

* Sources of data : U. S. Bur. Mines, *Minerals Yearbook, 1940*, p. 908; *Monthly Coke Rept.* 169 (1942), suppl. p. 4, 181 (1943), suppl. p. 5. U. S. Tariff Commission, *Rept.* 148, 2nd series P6.
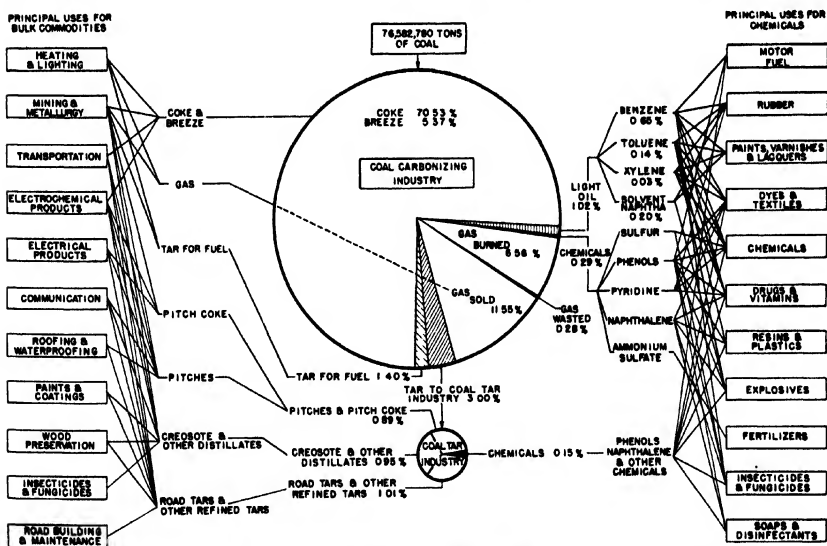
FIG. 9. Distribution of products resulting from the carbonization of coal in byproduct ovens in the United States in 1940. (Based on *Minerals Yearbook*, 1940, and U. S. Tariff Commission, *Synthetic Organic Chemicals*, 1940.)
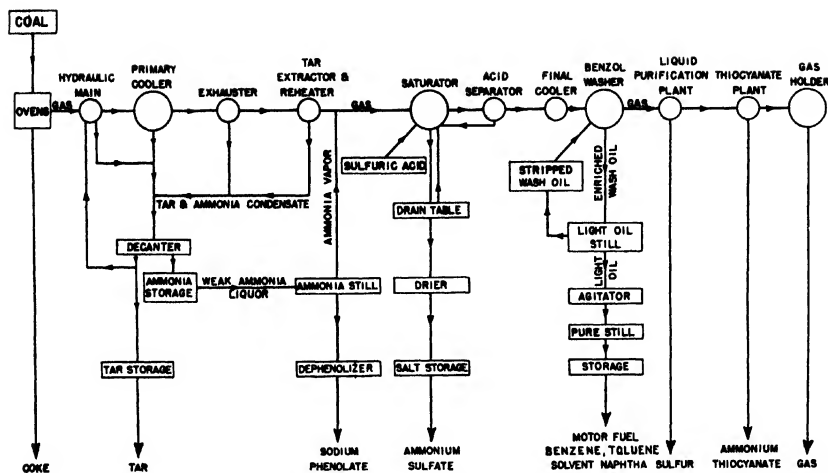
Fig. 10. Condensing and collecting system of a modern byproduct coke plant.

In spite of the fact that the points at which the tar and light oil are removed from the gas are widely separated and that one or more treatments of the gas may intervene, there is considerable overlapping of the constituents of coal tar, light oil, and gas. Coal tar usually contains small amounts of many or all of those substances of which light oil is principally composed; light oil contains small amounts of many compounds that are found principally in coal tar and also substances that are present in greater concentrations in the coal gas; coal gas in turn contains some of the constituents of light oil and even traces of some of the constituents of coal tar as well.

The table at the end of this chapter lists 348 chemical compounds which, according to the authorities cited in the literature references, have been identified thus far in tar, light oil, and gas produced by coal carbonization. They are arranged in order of their boiling points, from hydrogen, with a boiling point of $-252.5°$ C, to picene, whose boiling point is $519°$ C. (Ammonium chloride sublimes at $520.0°$ C.) In Chapter 28, Glowacki has listed 112 constituents of light oil, the highest boiling of which, with the exception of sulfur, is 3,4-dimethyl phenol, boiling point $225°$ C, and the lowest boiling is hydrogen sulfide, boiling point $-61.8°$ C. Assuming the lowest-boiling constituent of coal tar to be benzene, boiling point $80.09°$ C, and the highest-boiling constituent of gas to be naphthalene, the overlapping compositions of gas, light oil, and tar may be as shown graphically at the top of the next page. The individual compounds in each range may be determined from the table at the end of the chapter.

It is obvious that the byproduct equipment of the coal-carbonization plant does not effectively fractionate the vapors from the ovens. Rather than fractionation, the recovery process is one of fractional condensation to obtain tar, light oil, and gas. Refractionation of any one of these materials will yield products rightfully belonging to the other two.
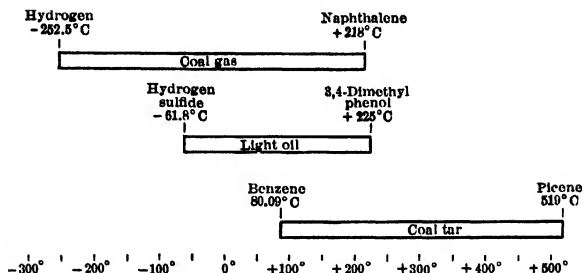
Even the recovery of the coal tar itself as ordinarily carried out at byproduct coke plants is a process of fractional condensation. The fractional condensers are the hydraulic and suction mains (A), the primary coolers (B), and the tar extractors or electrical precipitators (C). This is shown by Table XV, which gives the analyses of tar samples taken from the hydraulic and suction mains, the primary coolers, and the electrical precipitators of a typical byproduct coke plant. The analysis of the mixed tar (D) is also included. By calculation, the percentage of tar recovered from each

TABLE XV

ANALYSES OF TAR SAMPLES FROM DIFFERENT PARTS OF THE TAR-COLLECTING SYSTEM OF A TYPICAL BYPRODUCT COKE PLANT

	Source of Tar Sample			
	A Hydraulic and Suction Mains	B Primary Coolers	C Electrical Precipitators	D Mixed Tar Storage
Specific gravity at 15.5/15.5° C	1.216	1.152	1.135	1.195
Specific viscosity, Engler, 50 ml at 40° C	81.0	2.6	2.0	15.5
Benzene-insoluble material, weight percent	7.8	3.8	2.6	7.1
Distillation, weight percent				
to 170° C	0.3	0.5	2.1	0.9
200° C	0.5	2.5	6.6	1.3
210° C	1.0	6.5	15.0	2.3
235° C	3.7	22.3	30.0	10.8
270° C	9.0	33.2	37.6	19.5
300° C	14.2	37.5	41.7	24.1
315° C	16.7	39.6	44.2	26.0
335° C	20.9	42.5	46.6	29.8
355° C	27.3	47.3	51.0	36.8
Residue	72.3	52.4	48.5	62.8
Softening point of distillation residue (cube-in-air), °C	71.6	78.6	77.0	74.3
Tar acids, volume percent	1.61	2.5	2.0	1.25
Naphthalene, weight percent	7.0	26.0	28.0	13.0
Percent of total tar (calculated)	70.0	21.0	9.0	100.0

source in this particular plant is found to be as follows:

	PERCENT BY VOLUME
A. Hydraulic and suction mains	70
B. Primary coolers	21
C. Electrical precipitators	9
D. Total	100

By plotting the distillation results for A, B, and C as shown in Fig. 11, it becomes apparent that tar B contains tar of the same composition as tar A mixed with an oil distilling below 270° C, and the same is true of tar C.

The proportions and compositions of the oils which are mixed with tar A in tar B and in tar C, as determined by calculation, are given in Table XVI. The calculated analyses of the two oils are plotted as curves in Fig. 11, and curves also show how the calculated analyses for tar B and tar C compare with their analyses as determined by distillation. The calculated curve for tar B was obtained by adding distillation values for oil B to the distillation values for tar A in the proportion of 27 percent oil B to 73 percent tar A. Similarly, the calculated curve for tar C was obtained using 32 percent oil C and 68 percent tar A.

The proportions and compositions of the various tars covered by Tables XV and XVI are not necessarily the same as those from the same points in the tar-collecting system at some other byproduct coke plant or even from the same points at the same plant at some other time. The proportions of tars A, B, and C that go to make up the total mixed tar at a given coke plant and the composition of each may vary considerably, depending upon atmospheric temperatures, amount and kind of flushing used in the hydraulic main, and the extent to which the gas is cooled in the hydraulic main, primary coolers, and tar extractors or electrical precipitators. However, in general, the way and extent to which fractional condensation occurred in the byproduct coke plant discussed above is typical.

TABLE XVI

COMPOSITION OF TAR A FROM THE HYDRAULIC MAINS AS DETERMINED AND OF TARS B AND C FROM THE PRIMARY COOLERS AND ELECTRICAL PRECIPITATORS, RESPECTIVELY, AS DETERMINED AND AS CALCULATED BY ASSUMING THEM TO BE MIXTURES OF TAR A AND OF HYPOTHETICAL OILS B AND C

Distillate, weight percent	Tar A	Oil B	Tar B Calculated *	Tar B Determined	Oil C	Tar C Calculated †	Tar C Determined
to 170° C	0.3	0.8	0.4	0.5	6.3	2.2	2.1
200° C	0.5	8.3	2.6	2.5	21.3	7.2	6.6
210° C	1.0	22.7	6.9	6.5	49.0	16.3	15.0
235° C	3.7	76.9	23.5	22.3	92.0	31.9	30.0
270° C	9.0	100.0	33.6	33.2	100.0	38.1	37.6
300° C	14.2		37.4	37.5		41.7	41.7
315° C	16.7		39.2	39.6		43.4	44.2
335° C	20.9		42.3	42.5		46.2	46.6
355° C	27.3		46.9	47.3		50.6	51.0
Residue	72.3		52.8	52.4		49.2	48.5

* 73 percent tar A + 27 percent oil B.   † 68 percent tar A + 32 percent oil C.
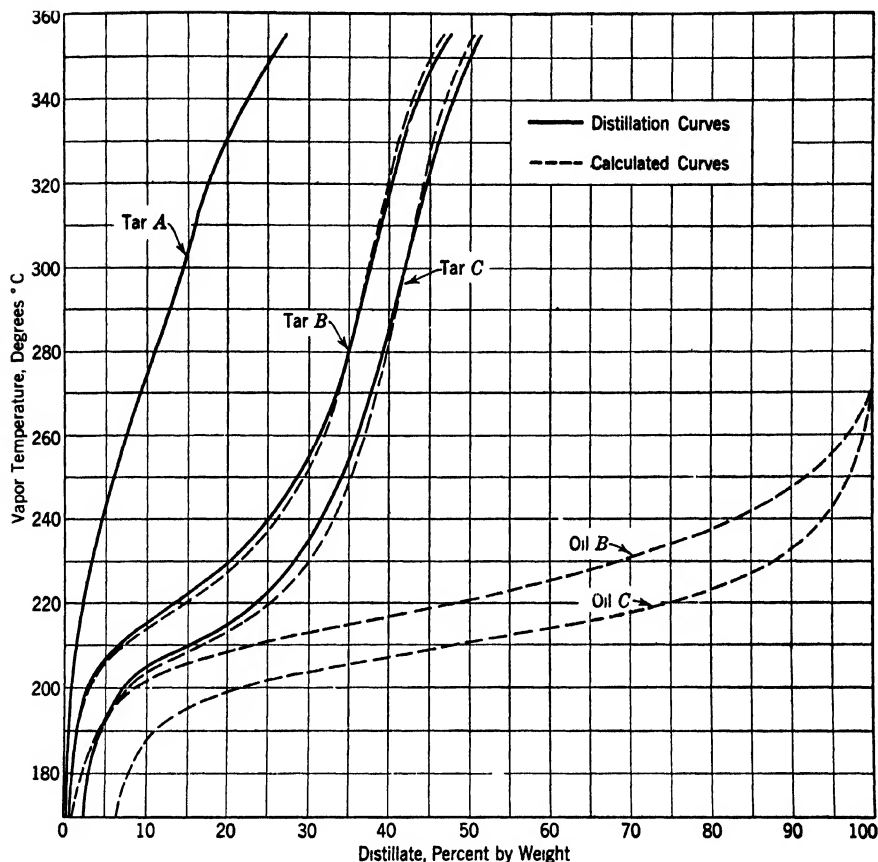
Fig. 11. Distillation curves determined for tar A (hydraulic and suction mains); tar B (primary coolers); and tar C (electrical precipitators); also distillation curves calculated for oil components of tar B and tar C and the distillation curves calculated for mixtures of tar A with oils B and C to duplicate the curves determined for tars B and C.

The fact that tar of the same composition as that condensed in the hydraulic and collecting mains is a principal constituent of the primary cooler tar and of the tar extractor or precipitator tar as well confirms the statement made by Wagner [37] that "gas produced during the carbonization of coal is a mixture of fixed gases, vapors of vari-

ous kinds, and, at times, also globules of liquids which are held in suspension, and are thus carried forward by the gas; these gases and vapors also carry forward some solid carbon in the shape of dust."

It appears evident that the products leaving a byproduct coke oven are tar or pitch globules suspended in the gas as a tar fog, vapors of condensable materials, noncondensable gases, and solid particles

[37] Wagner, F. H., *Coal Gas Residuals,* McGraw-Hill Book Co., New York, 2nd ed., 1918, pp. 1–2.

such as coke dust, coal dust, and lamp-black. The solid particles and a large part of the tar globules or fog drop out of the gas in the hydraulic and suction mains owing to the scrubbing and cooling action of recirculated tar or ammonia liquor. Further cooling of the gas in the primary coolers removes a second portion of the tar fog and condenses a part of the vapors. The remainder of the tar fog is finally removed in the tar extractors or electrical precipitators together with an additional amount of condensed vapors. There appears to be little or no difference in the composition of the tar globules that make up the tar fog at any point in the collecting system where they are removed.

TAR DISTILLATION

The fact that some fractional condensation occurs in the tar-recovery system of a byproduct coke plant suggests the possibility of recovering commercial products such as pitch, road tars, and creosote directly from the gas instead of the mixed tar that is usually collected. A process of this kind, developed by Feld, has been described in several United States patents[38] and in detailed reports by several authors.[39] Wagner described the Feld process in part as follows:

The gases coming from the benches or the coke ovens, as the case may be, are protected against condensation by wholly or partially insulating the hydraulic main and pipe connections so that the temperature of

the gas does not drop below the point at which tar products of low boiling point are separated. For the removal of the other tar products, Feld employs his centrifugal washer; in these washers progressive cooling, or progressive cooling combined with progressive washing, is attained through a progressive drop in temperature, and in this manner various tar products are obtained and separated from each other through the medium of the heat of the gas itself.

Although the Feld process was tried at several plants in Europe between 1906 and 1914, it did not meet with general acceptance there and is not used in the United States.

A direct recovery process tried in the United States but no longer in use has been described in numerous patents assigned to the Barrett Company. Some of them are listed in a report by Miller[40] which also included a detailed account of the process.

Cooke[41] commented as follows on the Barrett and Feld processes in particular and fractional recovery processes in general:

The Barrett processes have as their fundamental principle the utilization of the sensible heat of carbonization gases for the purposes of tar distillation and the direct fractional recovery of tar constituents from the crude hot gases.

Fractional recovery of tar products is by no means a recent discovery, Feld[12] having patented a process for condensing dry tar from hot gases by tar sprays in 1905. Later, in 1907, Feld[43] was granted a patent covering the use of a series of scrubbers, through which the gases were passed, a suitable drop in temperature being produced in each scrubber, and the scrubbing agents being suitable condensates from the process.

Burstall[44] invented a process, using a series

[38] Feld, W., U. S. Pats. 764,443 (1904), 792,-889, 806,467 (1905), 829,261, 832,466, 837,045, 839,741 (1906), 851,349 (1907), 922,409, 927,-342, 940,103 (1909), 951,778, 965,147 (1910), 983,037, 985,667, 1,011,043 (1911), 1,020,168 (1912), 1,110,914 (1914).

[39] Feld, W., Z. angew. Chem., 25, 705–11 (1912). Wagner, F. H., pp. 2–4, 17–32 of ref. 37. Raschig, F., Z. angew. Chem., 33, 260–2 (1920). Funcke, W., Glückauf, 60, 835–40, 868–76, 897–905 (1924).

[40] Miller, S. P., J. Franklin Inst., 215, 373–99 (1933).

[41] Cooke, F., Gas World, 92, No. 2378, Coking Sect., 13–6 (1930).

[42] Feld, W., Brit. Pat. 26,262 (1905).

[43] Feld, W., Brit. Pat. 20,139 (1907).

[44] Burstall, F. W., Brit. Pat. 6,508 (1910).

of static or centrifugal extractors, in which the gas was washed by circulation of tar, the extractors being maintained at suitable temperatures for the tar fraction desired. In 1913, Fischer[45] was granted a patent covering the use of hollow plate condensers of small cross-sectional area, the cooling medium being hot vapors or hot air. Means were provided for reducing the cooling medium to the desired temperature. Davidson[46] suggested intermittent distillation of tar in the hydraulic mains of Dessau vertical retorts and of coke ovens in 1914. Fractional distillation to pitch and oils was suggested in a paper of Purves[47] in 1916, the process proposing the use of oil sprays as condensing equipment, under suitable temperature conditions. The use of a series of contiguous cooling chambers, in which the gas does not come into contact with the cooling medium, followed by a series of filtering treatments, was patented by Umsted.[48] Chur[49] described a somewhat complicated system of fractional condensation with simultaneous distilling and refluxing of the condensate into the hot gas stream.

Cooke,[50] himself, invented a process for the direct recovery of road tars and oils from coal-carbonization gases. The following description of one application of his process has been taken from one of his patents:[51]

Road tar is prepared directly in and from the coke-oven plant by drawing it from the air-cooled main at a point before the gases reach the apparatus for extracting the tar of lesser density, and by maintaining the gases leaving the air-cooled main at a temperature above the dew point of the lighter tars contained in the gases, such temperature preferably varying between 160 and 190° Centi-

grade according to the density of road tar required.

Cooke's process is used to only a limited extent in England and is not employed in the United States.

The practice at coal-carbonization plants in this country is to collect the coal tar from the various points of the condensing system, decant it continuously to remove most of the ammonia liquor with which it is mixed, and transfer it to storage tanks from which it is pumped or otherwise transported to open-hearth furnaces or boilers if it is to be used for fuel, or to a tar-refining plant if it is to be distilled. The tar-distilling plant may be located at the coke plant where the tar is produced or at some place removed from the point of tar production.

Tar-distillation procedures at coke plants in the United States may be grouped generally according to the type of distillation residue made, as follows:

1. The distillation residue is a soft pitch of such consistency, when hot, that it can be used interchangeably with petroleum fuel oil in the liquid-fuel-burning equipment of an open-hearth furnace or boiler installation.

2. The residue is a medium grade of pitch which must be fluxed with undistilled tar, with tar oil, or with a suitable petroleum residual before it can be handled by fuel-oil-burning equipment.

3. The residue is hard pitch and may be granulated or flaked and added to coal charged into coke ovens where it replaces a part of the coal and is converted into coke.

In almost all tar still installations at coke plants in the United States, continuous tube or pipe stills are employed. They are especially suitable for any given coke plant where a large volume of tar of uniform

45 Fischer, J., Brit. Pat. 21,290 (1913).

46 Davidson, W. B., Gas World, 60, 523–7 (1914).

47 Purves, G. T., J. Soc. Chem. Ind., 35, 779–83 (1916).

48 Umsted, F. A., Brit. Pat. 135,931 (1918).

49 Chur, E., Ger. Pat. 383,793 (1923).

50 Cooke, F., Gas World, 92, No. 2378, Coking Sect., 13–6 (1930), 98, No. 2544, Coking Sect., 50–6 (1933), 114, No. 2592, Coking Sect., 21–4 (1941).

51 Cooke, F., Brit. Pat. 301,645 (1927).

composition is to be distilled to a single grade of residue.

Tube stills now in use at coke plants may be divided into the three following types:

✔1. The tar under pressure is pumped, at high velocity, through fire-heated tubes, discharges into a flash box from which the vapors pass to condensers or fractionating columns, and the pitch runs continuously to receiving tanks. Stills of this type have been discussed by several authors [52] and are described in numerous United States and foreign patents.

2. Pitch from the flash box of a tube still, operated in the manner described above, is drawn continuously into a vacuum box in which additional vapors are removed. Tube stills of this type are described by Miller [52] and by patents issued to MacCubbin and Zavertnik.[53]

3. Tar is mixed with a part of the pitch from a tube still. The mixture of pitch and partially distilled tar is then circulated through the tube still to a flash box where a part of the pitch is removed, and the remainder, mixed with more tar, is recirculated through the tube still. A still of this type developed in England and recently installed at a few coke plants in the United States has been discussed by several au-

thors [54] and in several patents to Wilton.[55]

The distillates removed from tars distilled at coke plants in the United States are, in some cases, processed there for the recovery of naphthalene, tar acids, and creosote. In other cases the total distillate is shipped to commercial tar-distilling plants for further processing.

European practice in tar distillation at coke-oven plants has been discussed in detail by Gluud and Jacobson; [56] numerous literature and patent references are cited by these authors.

Commercial tar-distilling plants in the United States employ tar stills of various types. Both continuous and batch stills are used. Continuous stills are usually employed at those plants where large volumes of tar are to be distilled to a single grade or to a few different grades of residue. Batch stills are generally employed at plants where small quantities of tar are handled or where frequent changes in the grade of residue are required.

In 1932 Weiss [52] presented a paper which was "intended to give a rather broad survey of the development of methods for the distillation of coal tar with especial reference to United States practice." At an earlier date (1926), Weiss [52] presented a report entitled "Tar Refining and Tar Products" to the American Gas Association. The information contained in these two papers dealing with the underlying, fundamental facts about tar distillation in general, and the descriptions and discussions of continuous and batch methods of

52 Weiss, J. M., *Tar Refining and Tar Products*, American Gas Association, New York, 1926, 32 pp.; *Chemistry & Industry*, **51**, 219–23, 246–50 (1932). Miller, S. P., *J. Franklin Inst.*, **215**, 373–99 (1933). Eisler, O., Zamrzla, Z., and Weinkoff, M., *Glückauf*, **72**, 184–8 (1936). Phillipson, G. A., *Chemistry & Industry*, **56**, 193 (1937). Shatwell, H. G., *ibid.*, **56**, 155–9 (1937). Adam, W. G., and Potter, F. M., *ibid.*, **56**, 193–4 (1937). Prüfer, G., *Tech. Mitt. Krupp*, **5**, 40–3 (1937). Fritz, W., *Teer u. Bitumen*, **35**, 107–9 (1937). Kuznetsov, M. I., and Belov, K. A., *Coke and Chem.* (*U.S.S.R.*), **6**, No. 12, 27–32 (1936); *Chimie & industrie*, **38**, 671 (1937). Grounds, A., *Gas World*, **109**, 77–80 (1938).

53 MacCubbin, A. A., and Zavertnik, J., Brit. Pats. 318,897, 346,407 (1928); U. S. Pat. 2,029,-883 (1936).

54 Anon., *Gas J.*, **204**, 773–6 (1933). Kernon, D. R., *Gas World*, **109**, 184–8 (1938). Rowley, E. H., *ibid.*, **116**, No. 2996, 5–6; No. 3001, 12–3 (1942). Sockett, C., *ibid.*, **116**, No. 3013, Coking Sect., 6 9 (1942).

55 Wilton, T. O., Brit. Pats. 337,581 (1929), 424,645 (1935); U. S. Pats. 2,260,071–2, 2,266,-698 (1941), 2,292,256 (1942).

56 See pp. 770–808 of ref. 7.

tar distillation employed in the United States at the times when the reports were written, are sufficiently complete that they need not be repeated here. Since 1932 such changes as have been made in distillation practices have had to do mainly with improvements in the design and operation of tube stills, some of which have been discussed above; the substitution of tube stills for direct recovery stills at coke plants; and the increased distillation of coal-tar pitch to coke in byproduct coke ovens according to a process developed by the Koppers Company [57] in which molten, high-melting-point coal-tar pitch is introduced gradually into byproduct coke ovens where it is distilled, carbonized, and devolatilized, after which it is pushed in the same manner as coke made in byproduct ovens from coal.

The two articles by Weiss, mentioned above, reviewed some of the tar-distillation methods employed in other countries, but more detailed discussions of recent European practices are also available.[58] Earlier reviews have been presented in several books.[59]

COAL-TAR CRUDES

Commercial products from coal tar are of two types, namely, crudes or bulk commodities and chemicals.

The principal crudes or bulk commodities made from coal tar in the United States, and in other countries as well, are wood-preserving oils, road tars, industrial pitches, and pitch coke. Wood-preserving oils are distillates, and road tars, industrial pitches, and pitch coke are residuals resulting from the distillation of coal tar.

The principal chemicals produced from coal tar are naphthalene, the tar acids, and the tar bases. Naphthalene is obtained from tar oils by crystallization, tar acids by extraction of tar oils with caustic soda, and tar bases by extraction of tar oils with sulfuric acid.

The latest year for which the U. S. Tariff Commission has reported statistics for products made from coal tar is 1940. The quantities of products made, converted to gallons, and the percentages of the total that these quantities represent are as follows:

	PERCENTAGE OF TAR	GALLONS
Road tars	28.1	150,523,083
Pitch	26.4	141,416,400
Creosote	22.3	119,678,785
Other distillates	9.4	50,631,609
Crude and refined tars	5.6	29,933,152
Pitch coke	3.4	18,181,200
Naphthalene	3.5	18,780,882
Tar acids	1.3	6,887,837

The above figures are not strictly correct for coal tar because the road tars include products other than coal tar since road tars may contain fluxes and may be made wholly or in part from water-gas tar. However, with this reservation the statistics do give an indication of the relative proportions in which the products were made.

Inspection of these figures shows that the chemicals, consisting of naphthalene and tar acids, produced in 1940 accounted for only 4.8 percent of the total tar distilled. Productions of tar bases and other chemi-

[57] Rhodes, E. O., Volkmann, E. W., and Fitzpatrick, J. C., U. S. Pats. 1,942,978–80 (1934).

[58] Berger, *Asphalt Teerind. Ztg.*, **26**, 638–40 (1926). Sladkov, M., *J. Chem. Ind.* (*U.S.S.R.*), **4**, 964–74 (1927). Weise, E., *Montan. Rundschau*, **22**, 249–59 (1930); *Petroleum Z.*, **26**, 499–504 (1930); *Asphalt u. Teer*, **30**, 1147–9, 1169–70, 1232–5, 1287–92, 1312–5 (1930).

[59] Lunge, G., *Coal Tar and Ammonia*, D. Van Nostrand Co., New York, 5th ed., 1916, 3 vols. Malatesta, G., *Coal Tars and Their Derivatives*, E. & F. N. Spon, London, rev. ed., 1920, 530 pp. Warnes, A. R., *Coal Tar Distillation and Working-Up of Tar Products*, Ernest Benn, London, 3rd ed., 1923, 511 pp. Spilker, A., *Kokerei und Teerprodukte der Steinkohle*, Wilhelm Knapp, Halle, 5th ed., 1933, 198 pp.

cals were so small that they were not even included in government statistics. Creosote and other distillates, road tars, pitch, crude and refined tars, and pitch coke accounted for 95.2 percent of the total tar that was refined.

In the following section of this chapter it is pointed out that coal tar contains relatively few chemical compounds in sufficient concentrations to make their commercial recovery profitable, at least by present methods of recovery and for present markets. Because they comprise altogether only 15 to 25 percent of the total tar, the principal products of coal tar, at least from a volume standpoint, will continue to be crudes or bulk commodities like those listed above.

Figure 12 is intended to show the way in which the bulk commodities are produced from a typical byproduct coke-oven tar. The curve connecting zero percent distillate with 30 percent residue represents the level of the pitch in a tar still as distillation proceeds from the original tar, with no distillate removed, to pitch coke with 70 percent distillate removed. The curve was drawn by plotting the percent distillate removed for a typical tar against the consistency of the distillation residue, as determined by float test, or softening point. The entire area below the curve represents residues such as road tars, pitches, and pitch coke; the area above the curve represents distillates, the usual distillate fractions being represented by the areas
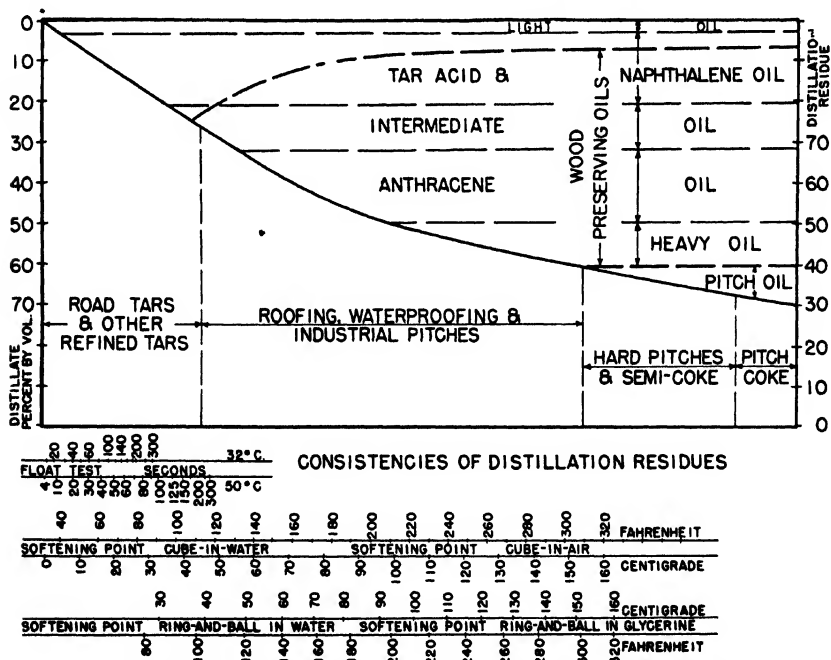
FIG. 12. Production of distillates and residues from a typical byproduct coke-oven tar.

between the parallel, horizontal, broken lines. The light-oil fraction, if recovered separately, would ordinarily be added to coke-oven light oil. Distillate in the area marked tar acid and naphthalene oil is the source of those chemicals and also tar bases when they are recovered. The intermediate oil contains small quantities of methyl naphthalenes, acenaphthene, and fluorene; and from the distillate in the area marked anthracene oil may be recovered anthracene, phenanthrene, and carbazole. The area between the two curves in the diagrams shows the amount of creosote of standard grade obtainable from the tar at each different consistency of the distillation residue.

Specifications and methods of test for several of the bulk commodities have been standardized by various national organizations; creosote by the American Wood Preservers Association, American Railway Engineering Association, and American Society for Testing Materials; road tars by the American Association of State Highway Officials and the American Society for Testing Materials; and roofing pitch by the American Society for Testing Materials. The proceedings of these various societies are replete with articles dealing with the materials which their specifications cover. General discussions of the properties and uses of bulk commodities from coal tar were given by Weiss [52] in 1926 and by Ramsburg.[60]

COAL-TAR CHEMICALS
With
JOHN O'BROCHTA *and* SUSAN E. WOOLDRIDGE

In the early days of coal carbonization, only coal tar was recovered from the gas. In 1845, Hofmann [61] proved the existence of benzene in the light oil derived from coal tar. It was this discovery which first established coal tar as a chemical raw material and laid the foundation for the so-called coal-tar chemical industry that was to follow. It was not until after 1876 that benzene was discovered in coal gas and the recovery of light oil as a source of benzene was started. Although light oil subsequently replaced coal tar as the principal source of benzene, coal tar continued to receive the credit for being the source, not only of benzene but of other light-oil constituents such as toluene and xylene and all the organic compounds derived from these components of light oil. Today perhaps 60 percent of all so-called coal-tar synthetic organic chemicals are derived from benzene, toluene, and xylene, and, although these parent substances come almost entirely from the light oil and not from coal tar, they are regularly classified as coal-tar chemicals. A better term would seem to be "light-oil chemicals."

True, coal-tar chemicals, at least from a commercial standpoint, are those whose parent substances occur principally in coal tar rather than light oil or coal gas. Although, as the table at the end of this chapter shows, hundreds of compounds have been identified in coal tar and undoubtedly many more will be identified especially in the higher-boiling fractions that have received comparatively little study to date, actually only a few are present in sufficient quantities to make their commercial recovery feasible, and still less are present in amounts sufficient to make their commercial recovery profitable.

Table XVII lists the constituents of coke-oven tar as determined by Weiss and Downs [62] in 1923. The authors commented on this table as follows: "The amounts

[60] Ramsburg, C. J., *Trans. Am. Inst. Mining Met. Engrs.*, **149**, 242–53 (1942).

[61] Hofmann, A. W., *Ann.*, **55**, 200–5 (1845).

[62] Weiss, J. M., and Downs, C. R., *Ind. Eng. Chem.*, **15**, 1022–3 (1923).

TABLE XVII

Constituents of Tar [62]

	Percent by Weight on Dry Tar
Light oil:	
Crude benzene and toluene	0.3
Coumarone, indene, etc.	0.6
Xylenes, cumenes, and isomers	1.1
Middle and heavy oils:	
Naphthalene	10.9
Unidentified oils in range of naphthalene and methylnaphthalenes	1.7
α-Monomethylnaphthalene	1.0
β-Monomethylnaphthalene	1.5
Dimethylnaphthalenes	3.4
Acenaphthene	1.4
Unidentified oil in range of acenaphthene	1.0
Fluorene	1.6
Unidentified oil in range of fluorene	1.2
Anthracene oil:	
Phenanthrene	4.0
Anthracene	1.1
Carbazole and kindred nonbasic nitrogen-containing bodies	2.3
Unidentified oils, anthracene range	5.4
Phenol	0.7
Phenol homologs (largely cresols and xylenols)	1.5
Tar bases (mostly pyridine, picolines, lutidines, quinolines, and acridine)	2.3
Yellow solids of pitch oils	0.6
Pitch greases	6.4
Resinous bodies	5.3
Pitch (460° F melting point)	44.7
Total	**100.0**

given should not be taken as commercially recoverable, as it would not ordinarily be practicable to refine oils to the extent necessary to obtain all of any given constituent." They also stated that "the most notable feature of the results is the compara-

tively few compounds existing in the tar in appreciable amount, probably not over one-quarter of those popularly supposed to be there."

Table XVII shows to what a small extent light-oil constituents are present in coal tar. By comparison with light oil itself, their concentrations are negligible. The true coal-tar constituents which were separated in sufficient amount to report individually in Table XVII are the following:

	Percent
Naphthalene	10.9
α-Monomethylnaphthalene	1.0
β-Monomethylnaphthalene	1.5
Acenaphthene	1.4
Fluorene	1.6
Phenanthrene	4.0
Anthracene	1.1
Carbazol and kindred nonbasic nitrogen-containing bodies	2.3
Phenol	0.7
Phenol homologs (largely cresols and xylenols)	1.5
Tar bases (mostly pyridine, picolines, lutidines, quinolines, and acridine)	2.3
Total	**28.3**

Even in the above table some mixtures rather than individual compounds are given (carbazol and tar bases), and as explained by the authors the quantities reported "should not be taken as commercially recoverable." For comparative purposes the analyses of two typical coke-oven tars are presented in Table XVIII. The tars were produced in the United States in typical byproduct coke-oven installations. The analyses were made by one of the principal tar-distilling companies in Germany in 1928 or 1929. The quantities reported were said to be commercially recoverable. It will be noted that including all chemical constituents the totals for these two tars were 16.5 and 18.7 percent, respectively.

TABLE XVIII

ANALYSES OF TWO TYPICAL COKE-OVEN TARS

	Tar 1	Tar 2
Benzene	0.293	0.079
Toluene	0.129	.....
Solvent naphtha	1.667	0.726
Cumarone resin	0.047	0.071
Benzoic acid	0.043	0.053
Phenol	0.861	0.469
Cresols	1.822	0.735
Pyridine	0.128	0.050
High-boiling bases	0.083	0.051
Naphthalene	4.801	8.273
β-Methylnaphthalene	0.142	0.300
Quinoline (technical)	0.247	0.236
Acenaphthene	1.129	1.510
Fluorene	0.902	0.847
Phenanthrene	2.900	3.388
Anthracene	0.705	1.157
Carbazole	0.623	0.706
	16.522	18.651
Light-oil constituents	2.179	0.929
True coal-tar constituents	14.343	17.722

Without including the light-oil constituents they were 14.3 and 17.7 percent. Truly, as Weiss and Downs pointed out, "The most notable feature of the results is the comparatively few compounds existing in the tar in appreciable amount · · · ."

Of the tar compounds listed in Table XVIII, those of greatest commercial importance at this time are naphthalene and the phenols (phenol, cresols, and xylenols). The light-oil constituents, though important, are obtained principally from light oil rather than tar. Also, pyridine, though important, comes principally from tar bases recovered from the gas by contact with sulfuric acid and to a minor extent from coal tar. Anthracene, formerly important as the source of anthraquinone derivatives, has now been largely supplanted by naphthalene, which, through conversion to phthalic anhydride, is a suitable source of the com-

pounds formerly derived from anthracene. Several general reviews of coal-tar chemicals have been published and are listed in the bibliography included in the final section of this chapter.

In order better to explain how the reputation of coal tar as a chemical raw material was established and to indicate its present and possible future position, some of the more interesting and important facts concerning its principal chemical compounds are reviewed in the following pages.

BENZENE

Benzene is included in this review because of its importance to the development of the coal-tar industry. The discovery of benzene or bicarburet of hydrogen, as he called it, was announced by Faraday[63] on June 16, 1825. He obtained it from the liquid deposited, under pressure, from illuminating gas made by dropping whale or cod oil into a furnace maintained at a red heat. He suspected that this bicarburet of hydrogen was present in coal tar but was unable to obtain it from that source. In 1834, Mitscherlich[64] obtained bicarburet of hydrogen by distilling benzoic acid with lime and proposed to give it the name benzin because of its relation to benzoic acid, which in turn derived its name from its original source, gum benzoin. Liebig objected to the name benzin and proposed that it be called benzole. The pure compound is now called benzene, and the name benzol is given to marketable products, prepared to trade specifications and containing high concentrations of benzene. The nomenclature of light-oil products has been discussed by Glowacki in Chapter 28.

[63] Faraday, M., *Phil. Trans.*, **115**, 440–66 (1825).

[64] Mansfield, C. B., *J. Chem. Soc.*, **1**, 244–68 (1849). Pope, W. J., *J. Soc. Chem. Ind.*, Jubilee No., **50**, 254–61 (1931).

The commercial recovery of benzene, or "benzole" as he called it, was developed by Mansfield and was described by him in 1849.[64] In his report to the Chemical Society of London he commented as follows on the usefulness of this substance:

It is possible · · · that this substance, either alone or mixed with the volatile fluids, may yet aspire to become, if not to receive, the "popularis aura." · · · The promises which benzole makes of utility are sufficiently numerous to encourage a belief that it may form a special object of manufacture and commerce. It may be procured to any extent from coal tar or from the light naphtha, in which it has hitherto been "wasting its sweetness on the desert air." If absolute purity be not required, it may be prepared, with very little expense and trouble, either in the laboratory, or, on the large scale, in vast quantities, and by a farther slight outlay of time, any required degree of purity may be ensured in the product.

To what extent benzene became or received the "popularis aura" as predicted by Mansfield may now be judged by the fact that a large proportion of all the intermediates for coal-tar dyes and synthetic organic chemicals comes directly or indirectly from this one chemical. It was Perkin's discovery of mauve in 1856 that founded the coal-tar-dye industry of today. In attempting to make quinine from aniline he obtained, instead of quinine, a black product. "This was purified and dried, and when digested with spirits of wine gave the mauve dye." [65]

Perkin was persuaded by his friends to manufacture mauve commercially, but

in starting this manufacture, the first difficulty was to decide upon the source from which aniline could be obtained at a sufficiently low price. It was at once evident that indigo was by far too costly a product for this purpose. Attention was then di-

rected to the extraction of aniline from coal tar, but after very numerous experiments it was found that the difficulty of purifying it was too great, that it was not practical to prepare it at a reasonable price from this product. There was therefore but one source left, namely, nitrobenzol.

Nitrobenzol had been discovered in 1834 by Mitscherlich, having been made by him from benzoic acid. Nitrobenzol, in turn, had been converted into aniline by Béchamp, using a mixture of finely divided iron and acetic acid for the purpose. So Perkin, starting with benzene, derived from coal tar as pointed out by Hofmann and developed by Mansfield, made nitrobenzene according to a commercial method which he developed himself, involving the use of nitric acid; converted the nitrobenzene into aniline by Béchamp's method; produced aniline sulfate with sulfuric acid and by reacting the aniline sulfate with potassium bichromate obtained the "sooty-black powder" which he digested first with coal-tar naphtha to remove a "resinous substance" and then extracted with "methylated spirits of wine" to obtain a solution which "when distilled left the mauve as a fusible bronze-coloured mass." [65]

This commercial venture of Perkin's converted coal tar "from a nuisance into a commercial article in great demand at good prices. Although only about 1 percent of the tar is obtained as benzol, this article at first yielded so much profit that the other products of tar distilling could be sold at low rates, and new markets could be opened out for them." [66] Today, as will be shown later, "the other products of tar distilling" have increased in importance, and benzol is derived principally from the light oil extracted from coal gas, having been discovered therein some time later than its discovery in coal tar by Hofmann, in 1845.

65 Perkin, W. H., *J. Roy. Soc. Arts,* **17**, 99–105, 109–15, 121–6 (1868–9).

66 Lunge, G., Vol. I, pp. 20–1, of ref. 59.

Between 1876 and 1883 papers by Berthelot, Bunsen, and Fischer referred to the presence of benzene in coal gas, but the exact date of its discovery therein is not known.[67] Had it not been for the presence of benzene in coal gas the development of many of our present-day commercial products from benzene would not have been possible, for the quantity of benzene obtainable from coal tar alone would have been entirely inadequate. Today a very small proportion of all the benzene used comes from this source.

NAPHTHALENE

Naphthalene

Although it was benzene which first established coal tar as a chemical raw material, benzene was not the first chemical substance discovered in coal tar, and no longer is it the most important chemical substance obtainable therefrom. Today, naphthalene, whose presence in coal tar was noted by Garden[68] and by Brande[69] in 1819, and studied and named "naphthaline" by Kidd[70] in 1821, holds first place.

The chemical composition of naphthalene was determined by Faraday in 1826. He prepared from it α- and β-sulfonic acids and "contributed further particulars concerning the behavior of this hydrocarbon."[71] "Ten years after its discovery, it

was still a matter of speculation whether naphthalene existed in coal tar, or was a product of its decomposition, till Laurent[72] decided the question." Thus wrote Mansfield[64] in 1849 and, to quote him further, "it may be useful to state that this interesting substance may be procured in enormous quantities at many of the tar works, where it is deposited, mixed with para-naphthaline (anthracene), by the oils distilled from the tar, in granular crystalline masses, called 'salts' by the workmen. It is there thrown away as useless, or, at best, burned for lampblack; and yet it is honoured in our chemical catalogues with a price of four or five shillings per ounce." Contrast the above with the production of 160,000,000 pounds of crude naphthalene in the United States in 1940 (Fig. 13). The value per pound was two cents or one-thousandth the price quoted ninety-one years before.

This enormous increase in the manufacture and use of naphthalene started in a very small way, with two coloring matters; one, for dyeing black on wool, was discovered by Roussin in 1861 and the other, called "Manchester yellow," was developed by Martius.[73]

Naphthalene had for many years been a nuisance in the gas industry. It was produced in immense quantities and had been thrown away. During the early history of the coal-tar colors, innumerable experiments were made with derivatives of naphthalene to produce coloring matters, but no results of any value were obtained; the experiments were mostly made with naphthylamine. In 1863 Perkin patented the first definite compound of the azo class shown to possess dyeing powers, namely amido-

[67] Berthelot, P. E. M., *Compt. rend.*, **82**, 871–5 (1876). Fischer, Ferd., *Dinglers Polytech. J.*, **249**, 178–82 (1883). Hoffert, W. H., and Claxton, G., *Motor Benzole, Its Production and Use*, National Benzole Assoc., London, 2nd ed., 1938, p. 3.

[68] Garden, A., *Ann. Phil.*, **15**, 74–5 (1820).

[69] Brande, W. T., *Quart. J. Sci., Lit., Arts*, **8**, 287–90 (1820).

[70] Kidd, J., *Phil. Trans.*, **111**, 209–21 (1821).

[71] Faraday, M., *Phil. Trans.*, **116**, 140–62 (1826); *Pogg. Ann.*, **7**, 104–12 (1826).

[72] Laurent, A., *Ann.*, **3**, 9–11 (1832).

[73] Perkin, W. H., *J. Chem. Soc.*, **69**, 596–637 (1896).
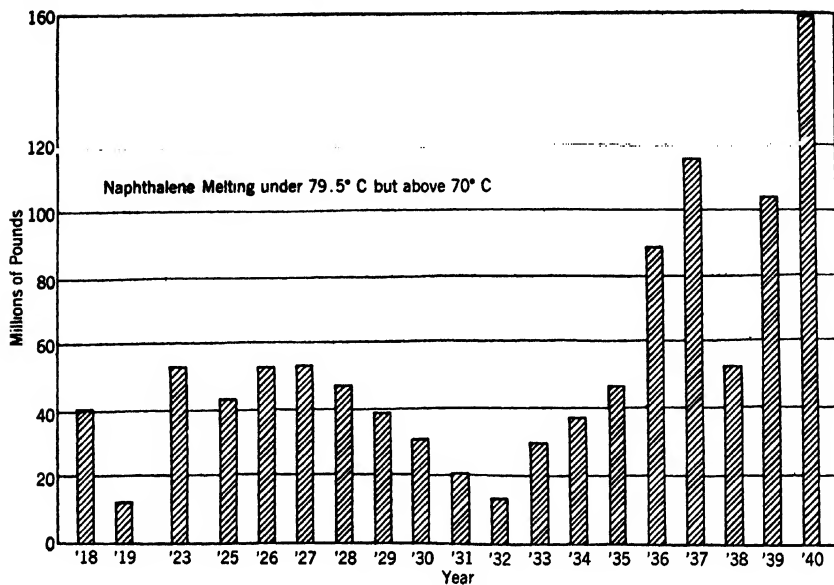
Fig. 13.   Naphthalene production in the United States, in millions of pounds, from 1918 to 1940. (Based on data from publications of U. S. Tariff Commission.)

azonaphthalene.[74]   This substance, however, was demonstrated to be of no practical value as a dye but has since been found of use in the preparation of the Magdala red which was discovered in 1867 by Schiendl.[73]

A principal development of the coal-tar colors has been in connection with diazo reactions, in which β-naphthol is used extensively.   One dye, which commanded great success, was known as Meister's scarlet and was produced by the action of diazoxylene chloride on the disulfonic acid of β-naphthol.   Substituted naphthalene derivatives of primary importance to dye manufacture are mainly the naphthols and amines and their sulfonic acids.

In 1868, owing to an increasing demand

74 Perkin, W. H., J. Soc. Chem. Ind., 4, 427–38 (1885).

for benzoic acid, experiments had been made with the view of obtaining it from naphthalene instead of gum benzoin.   Phthalic acid was first made from naphthalene and was then heated with lime, producing the calcium benzoate.[64]

Phthalic anhydride is largely employed as an intermediate for many of the most important dyestuffs.   These include principally those derived from anthraquinones and phthaleins.   The anthraquinones are the most important and are widely used for the manufacture of anthraquinone vat dyes and a number of alizarin dyes.   The discovery of phthaleins, which were among the first of the dyes derived from phthalic anhydride, dates back to 1871 and was the result of the investigations of Baeyer.   By "phthaleins" is meant the compounds formed by the union of a phenol and

phthalic acid or anhydride. The first of these discovered by Baeyer was gallein,[75] produced by heating pyrogallol with phthalic anhydride. Later the same year, he discovered fluorescein. Although it is not a very useful dyeing agent, Caro in 1874 found that fluorescein when brominated yielded eosine,[78] which was introduced into the market in July, 1874. The introduction of these coloring matters had a great influence on the manufacture of phthalic acid.

The manufacture of phthalic acid by the treatment of naphthalene with sulfuric acid was developed about 1896 for the manufacture of synthetic indigo and anthraquinone. Not long after, owing to an accidental discovery, this reaction was greatly accelerated by the use of mercury as a catalyst. The first large-scale technical synthesis of indigo resulted directly from this successful oxidation of naphthalene to phthalic acid. Since then a great deal of indigo has been made from phthalic acid through its intermediate, anthranilic acid. Apart from its use in the dye industry, phthalic anhydride was not widely employed until the Gibbs and Conover vapor-phase oxidation process,[76] with a vanadium catalyst, was begun in September, 1916. An important development from this outstanding process is the production of benzoic acid, a workable commercial process [77] being patented in 1925. However, the outstanding development has been the production of alkyd resins which have completely altered certain phases of the paint and varnish industry, especially in the field of quick-drying products.[78]

[75] Baeyer, A. von, *Ber.*, **4**, 457–9, 555–8 (1871).
[76] Gibbs, H. D., and Conover, C., U. S. Pat. 1,284,888 (1918).
[77] Daudt, H. W., U. S. Pat. 1,551,373 (1925).
[78] Durrans, T. H., *J. Soc. Chem. Ind.*, **61**, 211–4 (1942).

While the catalytic oxidation process for phthalic anhydride was developed for use by the infant dye industry in the United States during World War I, resins and esters are now a far more important outlet than dyes and intermediates, resins alone accounting for the major portion, with esters, dyes, dye intermediates, and miscellaneous uses following in order of their importance.

The alkyd (phthalic-glycerin) resins were first made about 20 years ago. As phthalic anhydride grew progressively cheaper, these resins became the subject of intensive research. They were modified with various drying and nondrying oils and with varying proportions of other constituents, resulting in an almost unlimited number of variations, ranging from viscous liquids to friable solids. These modified alkyd resins are used mainly as automobile and furniture lacquers.

Dibutyl phthalate had been the most widely used ester of phthalic anhydride. Its chief value is as a plasticizer in nitrocellulose lacquers and films, although it has interesting possibilities as a greaseless lubricant and in solvent recovery. Another ester, diethyl phthalate, is used as a fixative in perfumes, but chiefly as a denaturant of alcohol. It is also used as a plasticizer in cellulose acetate films. Other phthalic acid esters such as the dimethyl and diamyl phthalates have become of interest as plasticizers for a variety of synthetic resins. Dimethyl phthalate is also of special interest as an insectifuge.

Concurrently with the increasing uses for phthalic anhydride in dyes, resins, and esters there have been developed new processes for important products such as benzoic acid, phenolphthalein, anthraquinone and substituted anthraquinones, and benzoyl benzoic acid. The last is finding a

market in the form of its ethyl and methyl esters, as solid plasticizers which are characterized by compatibility with both nitrocellulose and cellulose acetate and by the high degree of water resistance which they impart to the film.[79]

Anthraquinone is manufactured by the Friedel-Crafts reaction of phthalic anhydride and benzene. The intermediate o-benzoyl benzoic acid has been separated and used as such or else dehydrated with sulfuric acid to form anthraquinone by ring closure. This dehydration step may also be effected with aluminum chloride, which avoids sulfonations but is not as economical as the sulfuric acid cyclization. The manufacture of anthraquinone by the above process is the result of the fortunate economical availability of aluminum chloride as well as phthalic anhydride. Many substitution derivatives of both phthalic anhydride and benzene have been subjected to analogous Friedel-Crafts reactions for the formation of substituted keto acids and anthraquinones.

In 1917, phthalic anhydride had an average market price of $4.23 per pound, the product being made by the sulfuric acid-mercury process. Subsequent annual increases in output together with process improvements resulted in lower and lower prices until in 1942 the price of phthalic anhydride was 14.5 cents per pound.

Naphthalene and its derivatives have come to be used in fields other than resins and dyeing. They are used in pharmaceuticals, explosives, perfumery, photography, and in synthetic tanning and wetting agents. As mentioned above, phthalic anhydride resins have revolutionized quick-drying finishes. In 1927, a systematic review of the chemistry of naphthalene and its derivatives was made by Reverdin, Nölting, and Van der Kam.[80]

As early as 1869, the best-known use had been found for naphthalene. In that year Markoe[81] suggested it as the best substitute for camphor for the protection of woolens from moths and other insects. He stated that "naphthaline has been put to a thorough test by Prof. Asa Gray in Harvard College Herbarium, and in the cabinets of the Boston Society of Natural History. The results obtained in these trials were highly satisfactory and conclusively proved the value of naphthaline as a protective agent against the ravages of the destructive insects that infest woolens and the cabinets of museums." He said further that "there is no demand for naphthaline in the American market, · · · it is very cheap, being a waste product in the distillation of coal tar for which no practical use has been found except for fuel and the manufacture of lampblack."

Naphthalene is recovered from coal tar by a variety of procedures, governed mainly by the nature of the tar, plant facilities, and demand and purity of naphthalene required. The initial step is batch or continuous distillation of the tar to yield a distillate which contains essentially most of the naphthalene and so-called salable tar acids and as little of the oils distilling beyond 235° C as is feasible. This distillate is known as crude naphthalene oil, tar acid oil, or middle oil.

When the tar is distilled by the batch process usually no fractionating column is used. A crude naphthalene oil is first obtained which is further redistilled, with or without the aid of a column, to produce a more concentrated naphthalene oil. The

[79] Caryl, C. R., *Chem. Industries*, **38**, 461–4 (1936).

[80] Reverdin, F., Nölting, E., and Van der Kam, E. J., *Tabellarische Übersicht der Naphthalinderivate*, M. Nyhoff, The Hague, 2nd ed., 1927.

[81] Markoe, F. H., *Proc. Am. Pharm. Assoc.*, **17**, 48–9, 365–6 (1869).

naphthalene oil can then be extracted with caustic soda solution to remove the phenols, after which it is allowed to crystallize, or the crystallization process may precede the caustic extraction.

In the continuous tar-still operation a fractionating column is used and the naphthalene or tar acid oil then proceeds directly to the crystallization process either before or after caustic treatment. In some plants the naphthalene fraction, from the continuous still operation, is extracted with caustic soda and then refractionated before entering the crystallization step.

The plant crystallization of crude naphthalene oil is generally known as the "panning" operation. Hot naphthalene oil is pumped into shallow rectangular pans where it is allowed to cool atmospherically and crystallize. The bulk of the contaminating oils are drained by gravity from the bottom of the pans. The drained "naphthalene cake" is then manually mined and "whizzed" in batch centrifuges to remove more of the contaminating oils. Washing of the cake in the centrifuge with hot water may be resorted to in order to improve the purity of the product. Other methods for removing contaminating oils from the drained "naphthalene cake" involve the use of hydraulic presses, generally steam jacketed, for manufacturing the purer grades of naphthalene. Such hot presses[82] are employed in Europe and to a limited extent in the United States.

The bulk of the naphthalene from the preceding operations is utilized directly, principally for the manufacture of phthalic anhydride, without any further purification. It is sold as crude naphthalene of specified freezing points, most frequently 74, 76, and 78° C. However, further purification is necessary for the manufacture of mothballs and certain chemicals.

A number of refining processes are in operation for this purpose. These processes vary, depending chiefly upon the ultimate purity of naphthalene desired. They include treating hot-pressed or centrifuged naphthalene with concentrated sulfuric acid,[83] caustic soda solution, charcoal, metallic sodium, and other agents,[84] and crystallization in the presence of water or aqueous solutions of reagents, followed by redistillation and possibly sublimation. Several of the processes are often combined, with purification by sublimation or distillation as the final step.

ANTHRACENE
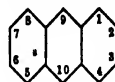
Anthracene

The first impetus to tar distilling was given by Perkin's discovery of aniline colors in 1856; a second and much needed boost was given when uses for anthracene were developed. Although only about 1 percent of the tar is obtained as benzene, it yielded at first so much profit that the other products of tar distillation could be sold at low rates and new markets opened out for them. Excessive competition reduced the price of benzene, and, as there was little sale of creosote oil and pitch, tar distilling seemed to be hardly a remunerative business. But, through Gräbe and Liebermann's discovery[85] of artificial alizarin, anthracene attained a much higher value

[82] Rosendahl, F., *Steinkohlenteer,* Theodor Steinkopff, Dresden and Leipzig, 1934, p. 94.

[83] Warnes, A. R., p. 322 of ref. 59. Hill, J. B., U. S. Pat. 1,819,680 (1931).

[84] Schroeter, G., U. S. Pats. 1,763,410 (1930), 1,800,159 (1931). Miller, S. P., U. S. Pats. 2,-078,963 (1937), 2,207,752 (1940), 2,257,616 (1941).

[85] Gräbe, C., and Liebermann, C., *Ber.,* 1, 49–51 (1868).

than any other product of coal tar and at the same time permitted the economical preparation of other coal-tar byproducts.

The history of anthracene begins in 1832 when Dumas [86] discovered it in coal tar. He first described it as "paranaphthalene." His work was confirmed [87] in 1857 by Fritzsche and in 1862 by Anderson, who also established the correct formula for anthracene. In 1868 Gräbe and Liebermann found that anthracene was formed from alizarin by the reducing action of zinc dust and that alizarin can be synthesized from anthracene.

At the time of this discovery, anthracene was not prepared by the tar distillers, as it had no application, and very little was known about it. Before alizarin could be manufactured, not only the best methods of getting it but also roughly how much could be produced had to be determined. Unless the hydrocarbon could be obtained in large quantities, artificial alizarin could not compete with madder. Perkin commenced by distilling pitch, but afterwards tar distillers were induced to try to separate it from the last runnings of their stills by cooling and then filtering off the crystalline products which separated out; the result was that in a short time such quantities came from this source that the distillation of pitch was abandoned.

The early industrial importance of anthracene is shown by the fact that the greasy material which in 1869 was burned in the furnaces or sold as a cheap wagon grease at the rate of a few shillings a ton received two years afterwards, when pressed into cakes, a price of no less than one shilling per pound. It is stated that an offer was once made, in the earlier stages of its history, by a manufacturer of anthracene to the Paris authorities to take up the "asphalt" used in the streets for the purpose of distilling it, in order to recover the crude anthracene. [88]

Production figures, at best, for anthracene are sketchy and incomplete. Suffice it to say that at first anthracene enjoyed a good price and increasing production until the cheaper method of anthraquinone manufacture from phthalic anhydride and benzene was developed. Since then only during the World War I has the recovery of anthracene from coal tar in the United States been appreciable.

Perkin first discovered that anthracene could be purified from the carbazole better by distilling with caustic potash than by distilling either alone or with caustic soda. This process of purification is still used today. Efficient fractional distillation has been developed by Kahl [89] for isolating from coal tar some of the more abundant compounds including anthracene. Winterstein and Schön [90] studied anthracene with a quartz lamp by the Tswett chromatographic adsorption analysis. The purification of coal-tar derivatives such as naphthalene and anthracene by crystallization from ethylene dichloride and naphtha has been effected by Boyd. [91] Solvent methods for the purification of anthracene were important at an early date and have continued to find favor to this day. The most common of these solvents were crude pyridine bases and solvent naphtha, although

[86] Dumas, J. B. A., *Ann. chim.*, **50**, 182–97 (1832); *Ann.*, **5**, 5–20 (1833).

[87] Fritzsche, J., *J. prakt. Chem.*, **73**, 282–92 (1857). Anderson, T., *J. Chem. Soc.*, **15**, 44–51 (1862).

[88] Roscoe, H. E., *Proc. Roy. Inst.*, **11**, 450–66 (1887). Gardner, W. M., *The British Coal-Tar Industry*, Williams and Norgate, London, 1915, 437 pp.

[89] Kahl, L., and Rütgerswerke A.-G., Brit. Pats. 208,691 (1923), 221,773 (1924); U. S. Pat. 1,742,258 (1930).

[90] Winterstein, A., and Schön, K., *Naturwissenschaften*, **22**, 237–8 (1934).

[91] Boyd, J. H., Jr., U. S. Pat. 2,163,581 (1939).

many other solvents have been proposed.[92] Another solvent, sylvan (2-methylfuran), has also been used to separate carbazole and anthracene.[93] The method outlined below for separating the anthracene, phenanthrene, and carbazole in anthracene paste has been described by a French patent.[94] Hydrogenation of anthracene paste was found to yield a product from which carbazole could be removed by filtration. Cooling the filtrate caused the separation of phenanthrene, which was filtered. Dehydrogenation of the second filtrate yielded anthracene. Polyakova[95] heated crude anthracene with maleic anhydride at 140 to 150° for 4 hours, taking advantage of the alkali solubility of the product formed to separate the anthracene, phenanthrene, and carbazole originally present. Several other investigations of the separation of these three tar constituents have been described.[96]

The forementioned anthracene purification methods serve but to illustrate the variety and extent of investigations to which the preparation of anthracene has been subjected.

The initial concentration of anthracene is made by distillation of coal tar. Batch or continuous distillation processes are used for the preparation of an anthracene or heavy-oil fraction. This fraction may vary widely in its composition but contains principally oils distilling from 300 to 360° C. The anthracene fraction is crystallized, centrifuged, and suction-filtered or pressed to produce a crude anthracene cake varying in composition from 10 to 35 percent anthracene, about half that amount of carbazole, and the remainder as phenanthrene, fluorenes, and other oils and solids. Preparation of anthracene from the crude cake now diverges into a variety of procedures such as those previously listed. A general method for the manufacture of anthracene of 80 to 90 percent purity involves recrystallization of the crude cake from various fractions of pyridine bases. The crude anthracene cake may be partially concentrated to 30 to 60 percent purity by solvent naphtha treatment, after which, by caustic fusion, hydrogenation, maleic anhydride addition, solvent treatment, or other processes, any desired purity may be attained.

92 Clark, J. M., Ind. Eng. Chem., 11, 204–9 (1919). Jaeger, A. O., U. S. Pat. 1,693,713 (1928). Norton, R. A., U. S. Pat., 1,764,031 (1930). Gluzman, L. D., Ukraïn. Khem. Zhur., 12, 349–66 (1937); Chem. Abs. 32, 3764 (1938). Grigor'ev, S. M., Trudy Khar'kov Nauch.-Issledovatel. Uglekhim. Inst., 1937, No. 8, 199–221; Khim. Referat. Zhur., 1, No. 7, 58–9 (1938); Chem. Abs., 33, 6029 (1939).
93 Pryanishnikov, A., Izmest'ev, P., and Kropotov, V., Trans. Inst. Pure Chem. Reagents (U.S.S.R.), No. 7, 129–30 (1939).
94 Compagnie des mines de Vicoigne, Noeux et Drocourt, Fr. Pat. 813,647 (1937).
95 Polyakova, I. M., Coke and Chem. (U.S. S.R.), 1938, Nos. 2–3, 75–81; Chem. Abs., 33, 3368 (1939).
96 Tsukerman, I., and Daeva-Stephanenko, I., Org. Chem. Ind. (U.S.S.R.), 3, 143–8 (1937).

COAL-TAR HYDROCARBONS DISTILLING BETWEEN NAPHTHALENE AND ANTHRACENE

1-Methylnaphthalene (α-methylnaphthalene)

Acenaphthene

(Fluorene) (diphenylenemethane)

Phenanthrene

The fraction of coal-tar hydrocarbons distilling between naphthalene and anthracene is the source of several potentially important industrial compounds. Although

the volume of oil in this range represents about a third of the total distillate usually obtained by the distillation of coal tar, it has been chiefly a component of creosote oil rather than the source of individual chemical substances. Such substances have commercial possibilities both from the standpoint of improved techniques for their preparation and for the discovery of new applications. Of the numerous hydrocarbons in this boiling range, the following are probably the more important: α- and β-methylnaphthalene, acenaphthene, fluorene, and phenanthrene.

Methylnaphthalenes. The methylnaphthalenes found in coal tar include the mono-, di-, and trimethyl homologs. Of the 26 methylnaphthalenes theoretically possible, 12 have been separated from coal tar, including the 2 monomethylnaphthalenes, 7 dimethylnaphthalenes, and 3 trimethylnaphthalenes. Of these only α- and β-methylnaphthalene have received any special attention, and that only to a limited degree. The others occur in difficultly separable mixtures or in insufficient quantities to warrant isolation.

Reingruber[97] attempted to separate the isomeric α- and β-methylnaphthalenes in 1881 and succeeded in establishing a partial characterization of their properties. He recognized that the β isomeride is a solid at room temperature and that the α compound is a liquid. The less-fusible β-methylnaphthalene can be obtained quite readily in a reasonably pure state by the usual methods of fractional distillation and crystallization. Early investigators, not having a good criterion of purity, erroneously assumed that separation of the β compound simultaneously yielded a mother liquor which was pure α-methylnaphthalene. In 1918, Weissgerber and Kruber[98]

noted that the separation was not so simple and that the ordinary grades of α-methylnaphthalene as then obtained were seldom even 50 percent pure. Wichelhaus[99] made somewhat better grades of the two compounds by the common method of recrystallization of picrates. The preparation of α- and β-methylnaphthalene by separation of their sulfonic acids is the subject of an 1897 German patent[100] and has been used since then by a number of investigators. A further improvement in the preparation of α- and β-methylnaphthalene from coal-tar oils developed with the realization that after removal of bases and acids from a narrow boiling fraction certain unsaturated compounds remain which will ultimately contaminate the α-methylnaphthalene. Coulson[101] overcame this factor in a somewhat laborious manner by treating the oils with sulfuric acid. Mair and Streiff[102] isolated the two monomethylnaphthalenes from petroleum and gave an excellent characterization of their physical properties.

The applications of α- and β-methylnaphthalene to industrial usage have been quite limited. As a crude mixture they have been suggested as diluents for cresol disinfectants.[103] α-Methylnaphthalene is used as a reference fuel in the determination of cetane and cetene numbers of Diesel oils,[104] and a 1927 German patent proposed using α-methylnaphthalene alone or with β-methylnaphthalene as a working medium for vapor engines.[105] Oxidation of

[97] Reingruber, F., *Ann.,* **206,** 367–80 (1881).

[98] Weissgerber, R., and Kruber, O., *Ber.,* **52,** 346–70 (1919).

[99] Wichelhaus, H., *Ber.,* **24,** 3918–21 (1892).

[100] Tammann, G., Ger. Pat. 95,579 (1897).

[101] Coulson, E. A., *J. Soc. Chem. Ind.,* **60,** 123–6 (1941).

[102] Mair, B. J., and Streiff, A. J., *J. Research Natl. Bur. Standards,* **24,** 395–414 (1940).

[103] Klarmann, E., and Shternov, N. A., *Ind. Eng. Chem., Anal. Ed.,* **8,** 369–72 (1936).

[104] Am. Soc. Testing Materials, *Standards,* 1942, Pt. 3, D613-41T, pp. 915–22.

[105] Siemens-Schuckertwerke A.-G., Ger. Pat. 467,664 (1927).

β-methylnaphthalene can yield 2-methyl-naphthoquinone-1,4 (vitamin K, active) whose mono sodium salt may be combined with phytyl bromide to yield the anti-hemorrhagic vitamin K.[106] One method of preparing α-chloromethylnaphthalene is the direct side-chain chlorination of α-methyl-naphthalene. This chloro compound may be cyanated and subsequently hydrolyzed to α-naphthyl acetic acid which has reported value in the stimulation of germination and growth in seeds, plants, and the like.[107] Methylnaphthalenes have unusual solvent properties, and development can be anticipated in this direction.

Synthesis of α-methylnaphthalene by the usual Friedel-Crafts or Würtz procedures has not been very successful. The β compound, however, is more amenable to such reactions.

Acenaphthene. Berthelot [108] first isolated acenaphthene from coal tar in 1867. A definite chemical formula for this compound was not established until 20 years later when Bamberger and Philip [109] proved the structure of naphthalic acid which had previously been recognized as a direct oxidation product of acenaphthene.

The general procedures for preparing acenaphthene from coal-tar sources are fairly simple. They consist of fractional distillation to obtain a close boiling cut from which the compound is separated by solvent treatment inasmuch as it has such excellent crystallizability. The solvent is often alcohol or some petroleum naphtha from which acenaphthene crystallizes in the form of long shining needles. However, the primary purification must be made by dis-

tillation in order to remove solid contaminants, mainly fluorene. According to a German patent,[110] this purification of ace-naphthene can be markedly increased by redistillation of crude acenaphthene in the presence of oils such as the dimethylnaph-thalenes. Methods like that of Nisembaum and Fedorova [111] are merely an elaboration on the usual distillation-crystallization pro-cedures except that more attention is given to securing better fractional distillation.

Everest [112] has comprehensively reviewed the chemistry of acenaphthene up to 1927.

The reactivity of the 7,8-positions of acenaphthene accounts for most of its es-tablished uses. Partial oxidation of the compound yields acenaphthequinone which, by partial reduction, may be converted to the mono ketone, acenaphthenone. The carbonyl groups of these ketones are very reactive to condensations and have resulted in the formation of several vat dyes. Among these dyes are the Ciba Scarlet, Orange G, and Red R. Other acenaph-thene dyes of interest are Alizarine Indigo B, which is prepared from 3-hydroxyace-naphthenone, and those derived from amino acenaphthenes.[113] Dziewonski and Rapalski [114] pyrolyzed acenaphthene and obtained acenaphthylene and lesser amounts of polymerized materials. Ace-naphthylene will polymerize at 90 to 100° C under thermal action alone, yielding higher condensation products and resinous sub-

106 Binkley, S. B., et al., *J. Am. Chem. Soc.*, **61**, 2558–9 (1939).

107 Cambron, A., U. S Pat. 2,304,537 (1942).

108 Berthelot, P. E. M., *Compt. rend.*, **65**, 465-507 (1867); *Ann. Suppl.*, **5**, 367–77 (1867–8).

109 Bamberger, E., and Philip, M., *Ber.*, **20**, 237–44 (1887).

110 Gesellschaft für Teerverwertung m.b.H., Ger. Pat. 277.110 (1913).

111 Nisembaum, S. I., and Fedorova, L. Y., *Coke and Chem. (U.S.S.R.)*, **9**, No. 10–11, 49–54 (1939); *Chimie & industrie*, **44**, 43–4 (1940).

112 Everest, A. E., *The Higher Coal Tar Hydro-carbons*, Longmans, Green & Co., London, 1927, pp. 1 57.

113 Morgan, G T., and Stanley, H. M., *J. Soc. Chem. Ind.*, **43**, 343-6T (1924).

114 Dziewonski, K., and Rapalski, G., *Ber.*, **45**, 2491–5 (1912).

stances [115] which have not yet materialized into any commercial importance. Exploratory attempts have been made in the condensation of acenaphthene with formaldehyde.[116] Oxidation of acenaphthene to 1,8-naphthalic acid offers possibilities for the industrial utilization of this hydrocarbon. The analogy between naphthalic and phthalic acids is such that the naphthalic may also find adaptations in the resin and dye industries. A review of the reported procedures for oxidizing acenaphthene to naphthalic acid would seem to indicate that a commercially feasible method is still wanting.

Acenaphthene and its derivatives have been studied for their effects on the initiation of growth and other responses in plants. Among these is 5-acenaphthene acetic acid.[117] Acenaphthene and 5-bromoacenaphthene were more recently shown to be effective in inducing abnormal mitosis in wheat.[118]

Fluorene. Fluorene was first obtained from coal tar by Berthelot at about the same time that he discovered acenaphthene.[108] The material which he prepared had a very pronounced fluorescence and was accordingly named fluorene. Hodgkinson and Matthews noted in 1883 [119] that further purification of fluorene causes a loss or lessening of the fluorescence which presumably is due to the presence of some higher-boiling fluorescent impurity. Barbier [120] improved somewhat the separation

method of Berthelot by more thorough fractional distillation but still had to use a noncommercial purification process which involved recrystallization of the picrate. One of the hydrogens of the fluorene methylene group was found to be susceptible of replacement by potassium or sodium by fusing a close-boiling fluorene cut with caustic potash; the fluorene was separated as a hydrocarbon-insoluble potassium salt which by hydrolysis regenerated the compound as a fairly pure material. Because of the losses due to rupture of the fluorene molecule as well as that of its principal contaminant, diphenylene oxide, less drastic fusion temperatures were sought for, using sodamide or sodium in the presence of ammonia or sodium in the presence of aniline or pyridine.[121] With the introduction of better fractional distillation equipment, the problem of producing commercial grades of fluorene has been largely reduced to distillation and solvent recrystallization.[122]

Fluorene may be considered as a dibenzo homolog of cyclopentadiene just as indene is benzocyclopentadiene. The methylene group in fluorene is less reactive than that of cyclopentadiene because of being masked by the adjacent benzo groups. However, it is this methylene group in fluorene which accounts for many of its reactions. Fluorene has been synthesized by the reduction of diphenylene ketone.[123] Among other syntheses of fluorene and its derivatives are those of Adam [124] from diphenyl and methylene dichloride and of Kliegl [124] which dealt with the ring closure of triphenyl carbinol to yield 9-phenylfluorene.

115 Dzlewonski, K., and Leyko, Z., *Ber.*, **47**, 1679–90 (1914).

116 Morgan, G. T., and Harrison, H. A., Brit. Pat. 319,444 (1928).

117 Zimmerman, P. W., and Wilcoxon, F., *Contrib. Boyce Thompson Inst.*, **7**, 209–29 (1935).

118 Shmuk, A., and Kostov, D., *Compt. rend. acad. sci. U.R.S.S.*, **23**, 263–6 (1939).

119 Hodgkinson, W. R., and Matthews, F. F., *J. Chem. Soc.*, **43**, 163–72 (1883).

120 Barbier, P., *Ann. chim. phys.*, [5], **7**, 479–540 (1876).

121 Gesellschaft für Teerverwertung, Ger. Pats. 203,312, 209,432 (1908).

122 Karpukhin, P. P., and Mikhajlenko, P. I., *Trudy Khar'kov. Khim.-Tekhnol. Inst. im. S. M. Kirova*, No. 1, 19–33 (1939).

123 Fittig, R., *Ber.*, **6**, 187 (1873).

124 Adam, P., *Compt. rend.*, **103**, 207–8 (1886). Kliegl, A., *Ber.*, **38**, 284–97 (1905).

Oxidation of fluorene gives fluorenone, which undergoes the general reactions of an aromatic ketone. A very excellent review of the various derivatives of fluorene and fluorenone is that of Rieveschl and Ray.[125] The derivatives include those formed by substitution in the ring and in the methylene group of fluorene and by condensation involving the carbonyl and the methylene groups. A number of dyes have been produced from both fluorene and fluorenone derivatives, but they have not yet materialized into important applications. Compounds from 2,7-diaminofluorene and 2,7-diamino-fluorenone have good possibilities as dye intermediates. They are generally of the tetrazo type. Derivatives of fluorene, particularly of 2,7-diaminofluorene, are used as analytical reagents.[126] The study of fluorene as an insecticide has been reported by Siegler, Munger, and Smith.[127] In 1939, interest was shown in the use of chlorofluorenes as insecticides. Condensations of fluorene to produce resins have not proved to be of any significant value as yet. Various amino alcohol esters of 9-hydroxyfluorene-9-carboxylic acid [128] and of fluorene-9-carboxylic acid [129] have been prepared which are reported to exhibit a very powerful antispasmodic effect and are free of the disadvantages associated with atropine or papaverine.

Another recently patented fluorene derivative, 9-fluorene-β-butyronitrile, is said to be useful for preparing drugs, plasticizers, and resins. Upon hydrolysis, it yields the corresponding amide or acid which may function as plant-growth hormones.[130]

Phenanthrene. The occurrence of phenanthrene in coal tar was discovered simultaneously in 1872 by Ostermayer and Fittig [131] and Gräbe.[132] A number of naturally occurring substances such as the morphine alkaloids, sterols, bile acids, and sex hormones contain the phenanthrene nucleus. Fittig and Ostermayer decomposed their new compound to diphenyl and thereby established some idea of its chemical nature. They called it phenanthrene in order to indicate its relationship to both diphenyl and anthracene.

Phenanthrene is found in coal tar in the anthracene fraction. It is considerably more soluble than anthracene in most organic solvents so that numerous attempts have been made to purify it by solvent crystallization alone. Clark [133] and others have pointed out that no solvent is completely effective and that chemical methods must be employed. Among the compounds associated with coal-tar phenanthrene are anthracene, carbazole, diphenylene oxide, and fluorene. Most attempts have been concerned only with the removal of anthracene and carbazole. Schmidt [134] tried to purify phenanthrene by selective oxidation of the crude material by which he converted the bulk impurity, anthracene, to anthraquinone. Clark [133] fused the crude phenanthrene with alkali in order to remove the carbazole. Clar [135] removed the anthracene by the 1,4 type of addition with maleic anhydride. Other procedures for the preparation of phenanthrene involve some degree of fractional distillation to con-

[125] Rieveschl, G., Jr., and Ray, F. E., *Chem. Revs.*, **23**, 287–389 (1938).

[126] Schmidt, J., and Hinderer, W., *Ber.*, **64**, 1793–6 (1931).

[127] Siegler, E. H., Munger, F., and Smith, L. E., *U. S. Dept. Agr., Circ.* **523** (1939), 9 pp.

[128] Wolfes, O., and Hromatka, O., U. S. Pat. 2,221,828 (1941).

[129] Burtner, R. R., U. S. Pat. 2,262,754 (1941).

[130] Bruson, H. A., U. S. Pat. 2,301,518 (1942).

[131] Ostermayer, E., and Fittig, R., *Ber.*, **5**, 933–7 (1872).

[132] Gräbe, C., *Ber.*, **5**, 861–3, 968–9 (1872); *Ann.*, **167**, 131–66 (1873).

[133] Clark, J. M., ref. 92.

[134] Schmidt, E., *Ber.*, **7**, 205–6 (1874).

[135] Clar, E., *Ber.*, **65**, 846–59 (1932).

centrate the product from which anthracene may be substantially removed by extraction from pyridine bases in which it is but moderately soluble,[92] reaction with maleic anhydride,[136] selective hydrogenation,[94] and others. Methods of removing carbazole include among others hydrogenation,[94] caustic fusion,[133] and formation of the carbazole sulfate.[137]

Preparation of pure phenanthrene from coal tar requires the removal of fluorene and diphenylene oxide as well as of carbazole and anthracene. Jeanes and Adams [138] removed these former by reaction with metallic sodium. The quantity of phenanthrene in coal tar has usually been reported by a method of differential analysis. Crude anthracene is analyzed for anthracene and carbazole, and the remaining material is assumed to be phenanthrene. Consequently, often enormous and exaggerated reports have been given of the amount of phenanthrene present in coal tars. This fact must be recognized and the amount determined by direct methods of analysis. Though not entirely satisfactory, the analytical method of Williams [139] and its later modifications are probably the best. In these procedures phenanthrene is oxidized to the quinone which is then isolated as a quinoxaline derivative.

A number of methods have been proposed for the synthetic preparation of phenanthrene, but most have shortcomings such as low yields or unsatisfactory purity. Among the better-known syntheses are the pyrolysis of cumarone and benzene,[140]

the dehydrogenation of stilbene,[141] and Pschorr's synthesis from o-nitrobenzaldehyde and sodium phenylacetate.[142]

Derivatives of phenanthrene have been obtained by the usual methods of substitution, hydrogenation, oxidation, condensation, and others, but none have acquired sufficient importance to cause any worthwhile demand for the hydrocarbon. Phenanthrenequinone is the principal derivative of interest. Quite frequently its preparation is attended by the degradation product diphenic acid. No important technical use has been found for phenanthrene. Despite the fact that a large number of dyes have been made from the compound, particularly the azo colors from the aminophenanthrenequinones, only one has attained any importance. This is flavinduline O, which is made by the condensation of phenanthrenequinone and o-aminodiphenylamine. Phenanthrene itself is used for the manufacture of lampblack.[113] At present very little phenanthrene is refined. The preparation of resins from this compound has not received sufficient attention to make them of any importance.

COAL-TAR HYDROCARBONS BOILING ABOVE ANTHRACENE
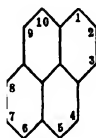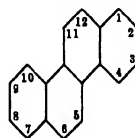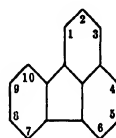
Pyrene   Chrysene   Fluoranthene

"Found in coal-tar fractions boiling above 360° C" is a frequently recurring expression of the chemical literature. It might almost be taken as an indication of the paucity of information on these fractions. No system-

136 Ardashev, B. I., and Polyakova, I. M., *Org. Chem. Ind. (U.S.S.R.)*, **4**, 601–5 (1937).

137 Weinmayr, V. M., U. S. Pat. 2,242,842 (1941).

138 Jeanes, A., and Adams, R., *J. Am. Chem. Soc.*, **59**, 2608–22 (1937).

139 Williams, A. G., *ibid.*, **43**, 1911–9 (1921).

140 Krämer, G., and Spilker, A., *Ber.*, **23**, 84–7 (1890).

141 Zelinsky, N. D., and Titz, I. N., *ibid.*, **62B**, 2869–73 (1929).

142 Pschorr, R., *ibid.*, **29**, 496–501 (1896).

143 Carpmael, A., Brit. Pat. 323,100 (1929).

atic approach to the industrial separation of hydrocarbons boiling above anthracene has as yet been reported. The fact that these hydrocarbons have extremely high boiling points, as far as organic compounds go, precludes their easy separation by the ordinary fractional-distillation methods. Chromatographic adsorption experiments have indicated still another obstacle, namely, the complexity of these higher "fractions." ·

About the only compounds of any industrial importance which have been obtained from coal-tar fractions boiling above 360° C are chrysene, pyrene, and fluoranthene. Although references to these compounds were made in the early years of the coal-tar industry, they have not received in any appreciable measure the consideration which has been given the lower-boiling components of coal tar.

Chrysene. Chrysene was discovered in coal tar by Laurent [144] in 1837. Its name is derived from the fact that, as prepared from coal tar, it has a golden yellow color. This color was shown by Liebermann [145] to be due to an impurity, chrysogen, which when completely removed left a colorless chrysene. A number of methods have been tried to remove this coloring impurity which seemed to be a relatively reactive substance. Liebermann used oxidation and reduction. Other methods have employed maleic anhydride [146] and partial sulfonation. In 1934, Winterstein and others, [147] by the utilization of chromatographic adsorption, were able to show that this coloring substance of crude chrysene was chiefly the hydrocarbon naphthacene which is a

very reactive benzo homolog of anthracene. This adsorption method consists essentially of passing a nearly saturated solution of the crude compound in a benzene-ligroin mixture through a tower packed with activated alumina.

Its slight solubility in most organic liquids has permitted the isolation of crude chrysene by solvent extraction. The classical method of Liebermann [145] and others proceeds by extracting the total coal-tar distillate which boils above the anthracene-carbazole range with carbon disulfide. In this manner pyrene, fluoranthene, methylanthracenes, methylcarbazoles, and other more soluble constituents are leached out, leaving a yellowish green crude chrysene. The crude chrysene is then recrystallized from boiling solvent naphtha or glacial acetic acid. Solvent treatment alone does not suffice to yield pure coal-tar chrysene. Other even less soluble compounds, such as chrysogen or naphthacene, impart yellow color to the chrysene and generally have to be removed by the previously mentioned chemical methods. Von Braun and Irmisch [148] claimed further that technically prepared chrysene from coal-tar sources contains up to 1.4 percent of sulfur in the form of sulfur compounds which need to be removed by combination with metallic sodium.

In 1874, Schmidt [149] utilized the formation of an insoluble double salt for the isolation of chrysene. Crude anthracene was simultaneously nitrated and oxidized with nitric acid. An insoluble crystalline dinitro-anthraquinone-chrysene compound was formed which, when reduced, released the chrysene in an easily separable state.

The boiling point of chrysene most frequently reported is near 450° C at atmos-

[144] Laurent, A., *Ann. chim. phys.*, (2), **66**, 136–213 (1837).

[145] Liebermann, C., *Ann.*, **158**, 299–315 (1871).

[146] Clar, E., and Lombardi, L., *Ber.*, **65**, 1411-20 (1932).

[147] Winterstein, A., Schön, K., and Vetter, H., *Z. physiol. Chem.*, **230**, 158–69 (1934).

[148] Von Braun, J., and Irmisch, G., *Ber.*, **65**, 883–7 (1932).

[149] Schmidt, E., *J. prakt. Chem.*, **117**, 241–89 (1874).

pheric pressure. Because of its high boiling point the most recent work on chrysene separation has concerned itself with high-vacuum fractional distillation or hydrogenation of low-melting coal-tar pitch. A number of German patents make use of soft pitch from coal hydrogenation, which is subjected to further hydrogenation and subsequent distillation.[150]

Among the synthetic preparations of chrysene, that of Spilker[151] in 1893 is particularly interesting. A United States patent issued in 1936[152] describes a modification of the same idea. Indene or hydrindene is passed over a dehydrogenation catalyst such as zinc oxide or magnesium oxide at a temperature of 500 to 700° C. The pyrolytic cracking of indene results in the evolution of hydrogen and the formation of chrysene in reportedly good yields. Another pyrolytic method of interest is that of Krämer and Spilker,[140] in which a mixture of coumarone and naphthalene was passed through a red-hot tube and a considerable amount of chrysene was formed.

The derivatives of chrysene have not been subjected to very extensive study. Probably the most important of these derivatives is 5,6-chrysenequinone, which was first prepared by Liebermann.[145] It is an ortho diketone and as such is subject to a number of interesting condensation reactions. Substitutions in the chrysene molecule by nitro, sulfonic acid, and halide groups has not achieved enough consideration to cause any worthwhile demand for chrysene for this purpose. Chrysene has sometimes been used purely for its fluorescent property. When pure, it exhibits a red-violet fluorescence; when crude, this color is masked by the golden-yellow of chrysogen.

Fluoranthene and Pyrene. Fluoranthene, or fluoranthrene as it is often named, is generally associated with pyrene because both are found in similar coal-tar fractions. Its original preparation and nomenclature are attributed to Goldschmidt[153] in 1877. He called it idryl. The present name of fluoranthene comes from the word fluoranthrene, which was used to designate the relationship of this compound to fluorene and phenanthrene.

Pyrene was obtained in a crude state in 1837 by Laurent[144] from the same source as that from which he had isolated chrysene. Bamberger and Philip[154] are credited with revealing the chemical structure of pyrene by their method of stepwise oxidation with chromic acid and permanganate solutions. The ultimate purification of pyrene and fluoranthene has been made by the chromatographic adsorption method. In this manner certain of the coloring chrysogens are removed.

The original procedures of obtaining pyrene and fluoranthene from coal tar were concerned simultaneously with the isolation of chrysene. The carbon disulfide filtrate from the extraction of chrysene was evaporated to yield a low-melting solid which was then recrystallized from alcohol and the resulting crystals were converted into the picrates. Several recrystallizations of the picrate mixture gave the individual picrates of pyrene and fluoranthene. These were subsequently treated with ammonia to regenerate the relatively pure compounds. Later improvements by Fittig[155] and others consisted of vacuum fractional distillation of the same crude material into

150 I. G. Farbenindustrie A.-G , Ger. Pats. 654,-082 (1937), 654,791 (1938).

151 Spilker, A., *Ber.*, **26**, 1538–45 (1893).

152 Wulff, C., and Treppenhauer, M., U. S Pat. 2,056,915 (1936).

153 Goldschmidt, G., *Ber.*, **10**, 2022–30 (1877).

154 Bamberger, E., and Philip, M., *Ber.*, **20**, 365–71 (1887).

155 Fittig, R., and Liepman, H., *Ann.*, **200**, 1–21 (1880) ; *Ber.*, **10**, 2141–4 (1877).

two fractions. Further treatment then followed by recrystallization of the picrates of the individual fractions. Fluoranthene was obtained from the first and pyrene from the second fraction.

Kruber's method of 1931 [156] represents a great improvement in the extraction of pyrene and fluoranthene from coal tar. In his procedure the starting material was a coal-tar fraction which boiled from 370 to 390° C. This fraction was first washed free of acids and bases and was then diluted with a petroleum naphtha and treated with metallic sodium. Fluoranthene was deposited as a filterable sodium salt, the pyrene remaining unattacked. Hydrolysis of the salt was followed by vacuum distillation whereby tetrahydrofluoranthene was obtained. It was dehydrogenated to yield pure fluoranthene. The unreacted pyrene fraction was distilled and upon solvent crystallization gave pyrene. In 1941, Coulson [157] enlarged upon Kruber's procedure by placing greater emphasis on fractional distillation in order to obtain a narrower boiling cut before any subsequent chemical treatment. He also noted that an almost quantitative dehydrogenation of tetrahydrofluoranthene can be effected by the use of selenium.

According to a British patent,[158] pyrene can best be economically produced by using the products of the dehydrogenation of selected fractions of hydrogenated coals or coal tars. A typical starting crude would be a hydrogenated fraction boiling from 370 to 390° C at atmospheric pressure or from 250 to 280° C at 50 mm.

Neither pyrene nor fluoranthene has been synthesized by any procedure which attracts industrial consideration.

[156] Kruber, O., *Ber.*, **64B**, 84–5 (1931).
[157] Coulson, E. A., *Chemistry & Industry*, **60**, 699–702 (1941).
[158] Johnson, J. Y., Brit. Pat. 435,254 (1935).

Partial oxidation of fluoranthene converts it to fluoranthenequinone, which may be further oxidized to fluorenone carboxylic acid. A small number of derivatives of fluoranthene have been made, but very little commercial application has been found for them. A United States patent [159] of 1942 has claimed the manufacture of a number of fluoranthene derivatives which may be of value as dye intermediates.

Somewhat more research has been reported on pyrene than on fluoranthene chemistry but not enough to excite significant industrial interest. Aluminum chloride condensations of acid chlorides and pyrene give condensation products which are of use as vat dyes.[160] The oxidation products of pyrene which may be of importance are pyrenequinone and the naphthalene-tetracarboxylic acid.

✓ TAR ACIDS

Phenol
(hydroxybenzene)

o-Cresol
(2-methylphenol)

3,5-Xylenol
(3,5-dimethylphenol)
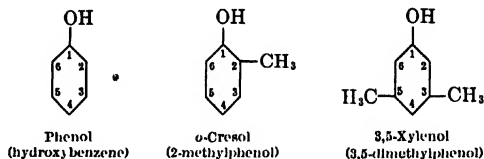
Tar acids is a general term including all the phenolic constituents of coal tar. The most important of these is phenol, the individual cresols and xylenols following in about that order. The fallacy, "Everything, even aspirin, comes from coal tar," owes much of its origin to the chemistry of tar acids, particularly because of the resins and drugs derived from phenols.

Phenol was discovered in coal tar by Runge [161] in 1834. He called it carbon-oil acid or carbolic acid, a name still quite

[159] Kern, W., Holbro, T., and Tobler, R., U. S. Pat. 2,292,691 (1942).
[160] Scholl, R., Ger. Pat. 239,761 (1910).
[161] Runge, F. F., *Pogg. Ann.*, **31**, 65–78, 513–24 (1834), **32**, 308–33 (1834).

commonly used. In 1841 Laurent[162] isolated "pure" phenol, which he called *hydrate de phenyle* or *acide phenique*. The present chemical name phenol was given by Gerhardt,[163] who had prepared it from salicylic acid.

The preparation of phenol from coal tar involves the simultaneous recovery of mixtures of the other tar acids. The basic principles generally applicable for the recovery of phenol and the other tar acids from coal tar include the following steps: (1) distillation of the tar to obtain an oil fraction boiling over a range which will include the commercially usable tar acids; (2) extraction of this fraction with caustic soda; (3) purification of the resultant caustic extract; (4) liberation of the tar acids; and, finally, (5) dehydration and distillation of the tar acids. Numerous variations and refinements occur within each of the preceding steps.

The tar may be distilled intermittently, with or without a column, or continuously with a fractionating column. A so-called tar acid oil or middle oil is collected which, depending chiefly upon the nature of the tar and the method of distillation, is generally from about 10 to 20 percent of the tar.

This tar acid oil is usually extracted with caustic soda, in concentrations varying from 8 to 50 percent, either before or after removal of the naphthalene, which, in most instances, is included in the tar acid oil fraction. The tar acids are thereby converted to the sodium salts, which are soluble in the aqueous, caustic layer. These soluble salts are collectively called sodium phenolate or sodium cresylate. Lime and other alkaline reagents have been used for this extraction process, but present practice prefers the caustic soda which Laurent

first proposed in 1841. The sodium cresylate is allowed to settle and is separated by gravity from the nonaqueous or "neutral oil" layer. In the early days of the tar acid industry, when fractional distillation equipment was crude, it was difficult to prepare pure phenol from the extracted tar acids. Consequently, attempts were made to concentrate phenol prior to distillation. Fractional saturation[164] was formerly practiced, in which insufficient amounts (based upon the total tar acid content) of caustic were used, whereby the more acidic carbolic acid was preferentially extracted along with somewhat less than the usual proportion of the other tar acids.

After separation, the sodium cresylate is freed of entrained and dissolved oils and bases. Among the processes which have been used for this purpose are aqueous dilution of the cresylate to throw dissolved oils out of solution and distillation to volatilize oils, bases, and some water and leave a concentrated cresylate. Current practice is evaporation under reduced pressure to controlled concentrations of sodium cresylate.

The next step in tar acid preparation is known as "springing," that is, the conversion of the tar acids from the sodium salts to the "free tar acids." This springing is generally effected by carbon dioxide, although sulfuric acid of varying strength may be used. At one time sulfurous acid was considered for this purpose.[165] The process of springing is not quite completed by treatment with carbon dioxide. After separation of the tar acids from the sodium carbonate solution by decantation, sulfuric acid may be added for more complete springing of the tar acids. The released tar acids are then separated by decanting

162 Laurent, A., *Ann. chim. phys.*, (2), **174**, 195–228 (1841).

163 Gerhardt, C., *Ann.*, **87**, 149–78 (1853).

164 Lunge, G., p. 733 of ref. 59.

165 Lowe, C., and Gill, J., Brit. Pat. 1,456 (1880).

from the aqueous sodium sulfate solution and are ready for dehydration and distillation. The spent sodium carbonate solution from the above springing operation is returned to a causticizing plant where caustic soda is regenerated by reaction with lime.

Subsequent refining of the tar acids involves intermittent or continuous distillation through a fractionating column whereby water is removed and various fractions may be taken such as crude phenol, crude cresols, and xylenols. Refractionation of these cuts can yield directly high-purity phenol and o-cresol. The remaining tar acids may be obtained as cuts having definite boiling ranges from which the individual components are separated by means other than fractional distillation.

The development of the tar acid industry paralleled the growth of phenol and was to a large extent dependent upon it. "The United States production of phenol prior to 1914 averaged about one million pounds a year and was entirely the natural product obtained from distillates of coal tar."[166] About four million pounds of phenol were imported annually from England and Germany. "During the World War large quantities of phenol were made synthetically from benzene for use as a raw material in the manufacture of explosives. At the close of the war it was estimated that domestic stocks of phenol, which were between 35 and 40 million pounds, would be sufficient for about three years' requirements."[166] "As a result the price dropped from about 45 cents to 6 cents a pound and the synthetic plants were closed."[167]

The limited quantities of phenol available to the synthetic resin makers prior to and during the [first] World War caused much concern to that industry and led to research work for substitutes, work resulting in the development of many new and modified types of resins in which tar acids other than phenol were used. But notwithstanding the uses of these other tar acids, the increased demand for synthetic resins used up the accumulated stocks of phenol sooner than expected.

Of the phenol produced in the United States from 1919 through 1923 a large portion was natural phenol but the rapid increase in demand and improvement of processes for synthetic phenol had by 1923 resulted in four companies beginning production of the synthetic article. The rapid increase in output, from about three million pounds in 1923 to about fifteen million pounds in 1925, was entirely the synthetic phenol. Since then a large part of the domestic production has continued to be synthetic although the production of natural phenol since 1935 has been about four times that of 1929.[166]

On the other hand, from the industrial viewpoint, the primary source of cresols and xylenols, unlike phenol, is still the crude tar acids which are derived from coal tar.

Although recognition had been made of the fact that cresols were present in crude tar acids, they were generally considered contaminants which had to be removed in order to prepare pure phenol. About 30 years after Laurent's isolation of "pure" phenol, Southworth[168] was able to state that "it would, therefore, appear that o-cresol is a constituent of the cresol from coal tar." However, it was not until 1878 that Tiemann and Schotten[169] and later others recognized that "cresol" from coal tar is in reality a mixture of three isomers.

o-Cresol, as previously noted, is prepared by fractional distillation of crude tar acids to obtain a concentrate which is then refractionated to yield a product of the desired purity. Because of this compara-

166 United States Tariff Commission, *Phenol,* 1928, p. 3.

167 United States Tariff Commission, *Synthetic Resins and Their Raw Materials,* Rept. 131, 2nd series, 1938, pp. 13, 111.

168 Southworth, M. S., *Ann.,* **168,** 267–76 (1873)

169 Tiemann, F., and Schotten, C., *Ber.,* **11,** 767–84 (1878).
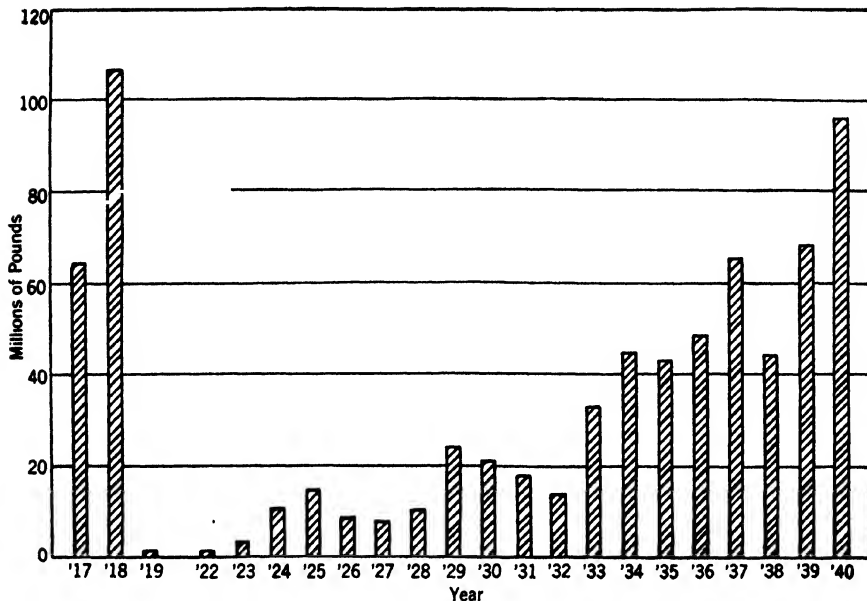
Fig. 14.   United States production of natural and synthetic phenol.   (From data contained in *U. S. Tariff Commission Reports* **131, 136, 140,** and **148.**)

tive ease of preparation, *o*-cresol was obtained from crude tar acids considerably sooner than the *m*- and *p*-cresols, which distil within a boiling range of about 1½°. This necessitated the discovery of some other means of separation than distillation. Subsequent research has evolved a number of chemical separation schemes for *m*- and *p*-cresol, but even at the present time these two compounds are still marketed almost entirely as a mixture.

In 1900, Raschig[170] attempted to make use of the different crystallizabilities of the *m*- and *p*-cresol sulfonic acids for this purpose. A German patent of 1902[171] employed oxalic acid for the separation procedure. Other early processes for meta-para separation were proposed which made

use of the formation of metallic salts and of acetyl, benzoyl, and other derivatives.

A number of patents on the separation of *m*- and *p*-cresol were issued in the 1930's. In 1937, two United States patents[172] dealt with modifications of the above-mentioned oxalic acid method. A commercial mixture of *m*-*p*-cresol addition compound was separated by crystallization and the *p*-cresol then released by hydrolysis. As described in a 1939 Japanese patent,[173] *m*-*p*-cresol mixture was treated with phosphoric acid to form the tar acid phosphates which were then separated by crystallization from petroleum ether and subsequently released by hydrolysis. Another recently developed method concerns the separation of the constituents of *m*-*p*-cresol mixtures

170 Raschig, F., Ger. Pat. 112,545 (1900).
171 Firma Rudolf Rütgers, Ger. Pat. 137,584 (1902).

172 Engel, K., U. S. Pat. 2,095,801 (1937). Gould, D. F., U. S. Pat. 2,099,109 (1937).
173 Kotake, M., Jap. Pat. 133,250 (1939).

by alkylation [174] with an olefin. A m-p-cresol fraction was treated with an olefin, such as isobutylene, upon which the isomeric phenols were dialkylated and separated by fractional distillation. The individual di-*tert*-butyl cresols could then be dealkylated to give refined m- and p-cresols.

At present only a small part of the m-p-cresol fraction of tar acids is used for the preparation of the individual isomers, and that mainly by the butylation or oxalic acid methods.

The study of xylenols as individual isomers occurring in tar acids had not received much attention before 1910. Schulze,[175] in 1887, noted the presence of the 3,5- and the 2,4-xylenols and the preponderance of 3,5-isomer in high-boiling tar acids. In 1912, Raschig [176] stated that all of the six possible xylenols are present in coal tar but that the 3,5-xylenol is the most abundant.

The most frequently referred to procedure for the separation of the specific xylenols was worked out by Brückner in 1928.[177] His method concerns separation of the xylenols by taking advantage of the different solubilities of the sodium salts in 25 percent sodium hydroxide and also of the specific splitting temperatures of the sulfonic acids of these xylenols. Kester [178] reported that 3,5-xylenol can be prepared by thorough fractional distillation of tar acids and subsequent petroleum ether crystallization of the 217 to 222° C. cut.

Further purification of this xylenol may be effected by Brückner's caustic precipitation method.

3,5-Xylenol is the only individual dimethyl phenol which has been prepared in any appreciable quantity from coal tar. It is made by fractional distillation and crystallization of tar acids boiling above the m-p-cresol range.

The major use of tar acids is in the manufacture of phenolic resins. Early developments on the production and use of phenolic resins were limited almost entirely to one tar acid, namely phenol. However, the diverting of phenol to military purposes during World War I promoted the investigation of certain fractions of tar acids, cresols, and xylenols as possible sources of resin-forming raw materials. Synthetic resins now form the chief outlet for both the cresols and xylenols as well as phenol.

Before the work of Baeyer in 1872 [179] on phenol-aldehyde condensations, practically nothing of importance had been done on the utilization of phenols for synthetic-resin manufacture. The phenolic resins were among the first true synthetic resins to appear commercially. They were preceded only by the semisynthetic products, celluloid in 1868 and casein plastics in 1890. In 1891, when formaldehyde became a commercial item, Kleberg [180] and others began to investigate seriously the reaction of phenol and formaldehyde in the presence of hydrochloric acid, bases, and other catalysts. The results were so satisfactory that thereafter phenol formaldehyde condensations were studied with renewed interest. Between 1900 and 1910 the studies increased not only from the standpoint of processes of manufacture but also in appli-

[174] Stevens, D. R., and Livingstone, C. J., U. S. Pat. 2,297,588 (1942). Stevens, D. R., *Ind. Eng. Chem.*, **35**, 655–60 (1943).

[175] Schulze, K. E., *Ber.*, **20**, 409–14 (1887).

[176] Raschig, F., *Z. angew. Chem.*, **25**, 1939–48 (1912).

[177] Brückner, H., *ibid.*, **41**, 1043–6, 1062–6 (1928); *Erdol u. Teer*, **4**, 562–4, 580–3, 598–602 (1928).

[178] Kester, E. B., *Ind. Eng. Chem.*, **24**, 770–1 (1932).

[179] Baeyer, A. von, *Ber.*, **5**, 25–6, 280–2, 1094–100 (1872).

[180] Kleberg, W., *Ann.*, **263**, 283–6 (1891), **264**, 351 (1891).

cations as substitutes for shellac and other natural resins. As in practically all fields, it is difficult, perhaps even superfluous, to assign categorically one man or process as the primary precursor of that field, but, by virtue of their subsequent commercialization, United States patents issued to Baekeland [181] became the basic patents on phenol formaldehyde resins, and Baekeland has generally come to be considered the founder of the phenolic resin industry. United States production of phenol formaldehyde molding compositions originally was practically restricted to one company, the Bakelite Corporation. However, in 1926 the original Baekeland patents expired, and since then a large number of other producers have been established with the consequent phenomenal development of the phenolic resin industry along with the younger alkyd resins.

The term phenolic resins was first applied to condensations of phenol and aldehydes but has now come to include the isomeric homologs of phenol, cresols, xylenols, and other high-boiling tar acids or any mixture of these materials. However, as late as 1937, about 66 percent of the United States production of tar acid resins was still made from phenol.[167]

In the condensation and polymerization of phenol and formaldehyde the first product formed is known as the A stage condensation product. It is usually a liquid or semisolid which on continued heating is converted to the B stage intermediate condensation product—a thermoplastic solid. The final C stage product is infusible; it is produced by the action of heat and pressure on the B stage product.

Tar acid resins find a great variety of applications, for molding, casting, laminating, surface coating, adhesives, and other

uses. Molding compositions may be made from mixtures of tar acids, but the present trend is toward the use of pure phenol itself inasmuch as better control may be had of purity and consequently of reaction. *o*-Cresol is of no value in molding compounds. *m*-Cresol, when it is eventually produced at a cheaper price, should find wider application in this field. Pure phenol is also used for cast resins. Laminating and coating resins as well as numerous other types of resins are made from mixtures containing varying amounts of cresols and xylenols manufactured to the buyers' specifications.

Another important application of tar acids in relation to the resin industry is in the manufacture of tricresyl phosphate. This material is made from tar acids and phosphorus oxychloride and utilizes any one of several marketed grades of cresol or cresylic acid. Tricresyl phosphate is used as a plasticizer for celluloid, cellophane, polyvinyl, and other resins.

The earliest use of tar acids or fractions of them was in the manufacture of disinfectants and disinfectant-containing products. Today the second major use of tar acid, in terms of tar acids consumed, is in the disinfectant industry. Lord Lister's application of phenol in 1867 [182] as a preventive of blood poisoning was the first specific use of phenol as an antiseptic. It was the standard chosen in 1903 in setting up the Rideal-Walker phenol coefficient test by which disinfectants are still rated. Although phenol was at one time widely used as an antiseptic and disinfectant, it has been largely displaced for these purposes by substituted derivatives and the other tar acids which are usually safer and have higher germicidal potency.

The most widely used type of disinfectant on the market today is that made by

181 Baekeland, L. H., U. S. Pats. 942,699, 942,809 (1909).

182 Macewen, W., *Nature*, **90**, 499–505 (1913).

the mixture of tar acids and soap solutions. The United States Bureau of Animal Industry specifies that permitted disinfectants shall contain less than 5 percent phenol. Standard saponified cresol solution, U.S.P., is compounded from U.S.P. grade of cresol, but other disinfectants may be made from a wide variety of tar acids as well as a diversity of saponifying materials. When made from cresols such disinfectants have a phenol coefficient of about 3 and about 5 when xylenols are used. Cresylic acid has been employed for many years in the manufacture of cresylic acid hand soaps. For these soaps relatively low-boiling tar acids, the cresols, are desirable. The higher-boiling acids are used in the preparation of wool scouring soaps.

Among the tar acid derivatives serving as antiseptics and disinfectants are the halogenated and nitrated phenols and cresols, butyl and other alkylated phenols and cresols, mercuriophenols, and a variety of others.

The synthesis of phenolic derivatives of pharmaceutical value has continually progressed since the development of phenol in commercial quantities. A major part of the early growth was due to Kolbe's [183] synthesis of salicylic acid from sodium phenolate and carbon dioxide. Salicylic acid is used itself or is converted into specific derivatives such as salol (phenylsalicylate) or aspirin (acetylsalicylic acid). In 1940, the U. S. Tariff Commission's report on synthetic medicinal products listed about 20 derivatives of salicylic acid. In that year aspirin and salicylic acid alone constituted more than 60 percent by weight of all the synthetic medicinals produced in the United States.

Trinitrophenol has accounted for much of the growth of the tar acid industry. In 1841, Laurent [162] nitrated phenol to trinitrophenol or picric acid, which he recognized as having explosive properties. This phenol derivative had some interest as a pale yellow dye for silk, but its instability limited its value. Shortly after 1885 when Turpin [184] discovered a practical way of utilizing picric acid as a military explosive, an added impetus was given to phenol production for the manufacture of picric acid as an explosive. The phenomenal increase in demand for phenol in the first part of World War 1 was due to the enormous requirements of picric acid, ammonium picrate, and to a lesser extent of chloropicrin.

Toward the end of the war picric acid was largely superseded by TNT, trinitrotoluene. Among other nitro phenols which are becoming increasingly important is dinitro-o-cresol, which is receiving considerable interest as an agricultural spray. It is used in the control of winter moths, plant lice, and leaf-sucking insects.[185]

The common coal-tar phenols and their substituted derivatives, unlike the naphthols, have only moderate applications as dyestuff intermediates. The presence of the phenolic hydroxyl group generally makes the dye highly sensitive to alkali, which necessitates the blocking or protection of this group in order to obtain a reasonably usable dye. One of the first phenolic dyes was aurine or rosolic acid. Phenols are used in the preparation of certain azo and phthalein dyes. It is interesting to note that the phenol-derived compound, salicylic acid, has been used for the preparation of about one hundred dyes, yet in the period 1936-7 only about 5 percent of the total phenol consumption of the United States was taken up by dyes and intermediates.[166]

[184] Turpin, E., Fr. Pat. 167,512 (1885); Ger. Pat. 38,734 (1886).

[185] Loewel, E. L., Gartenbauwiss., 16, 509-24 (1942).

[183] Kolbe, A. W. H., J. prakt. Chem., (2), 10, 89-112 (1874).

Alkylated phenolic derivatives are used in the petroleum industry. Diisobutyl phenol has been patented [186] as an anti-sludging agent for lubricating oils. 2,6-Di-*tert*-butyl *p*-cresol is used commercially as an antioxidant in gasoline [187] and other petroleum products.

<div align="center">

PYRIDINE BASES

</div>

<div align="center">

Pyridine   Quinoline

</div>
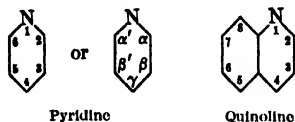
The name "pyridine bases" is generally meant to include pyridine and its alkyl homologs and also quinoline and alkyl quinolines, which are but benzo derivatives of pyridine itself. In a somewhat limited sense, the expression "tar bases" is synonymous with pyridine bases, principally because of the comparatively more abundant source of the pyridine bases in coal tar. In addition, aniline and homologs of the pyrrole series are also classed in the tar-base category.

Studies of the alkaloids are usually prefaced by a review of the chemistry of pyridine bases. Conversely, any consideration of the pyridine bases will also find it necessary to include the alkaloids, because some modifications of the pyridine or quinoline molecule are important constituents of many alkaloids. In fact, most of the bases found in coal tar have at one time been made from the alkaloids. Pyridine is frequently considered one of the simplest members of the alkaloid group. Of the more common alkaloids, nicotine from tobacco, piperine from pepper, and conine from hemlock contain the pyridine nucleus, whereas cinchonine and quinine of the cinchona group have the quinoline configuration.

Dry distillation of nitrogen-containing materials, such as the vegetable alkaloids and animal oils, led to the first recognition of volatile organic basic substances. The odorin which was separated from bone oil by Unverdorben [188] in 1827 was not characterized much beyond its obvious property of possessing a foul odor. In 1846 Anderson,[189] in studying naphtha from coal tar, isolated a base, by sulfuric acid extraction, neutralizing with ammonia and subsequent distillation, which he considered similar to odorin. A characterization of its properties caused him to believe that he had a pure compound. He called it picoline. It is quite likely that this material was a crude grade of α-picoline. None the less, this was the first reported instance of a systematic study of the pyridine molecule. The early literature on the pyridine bases is large because of their relation to the alkaloids; it has been summarized by Calm and von Buchka.[189]

Concurrently with his discovery of phenol in coal tar, Runge,[161] in 1834, also found three bases, one of which he called leukol. In 1842, Gerhardt [190] obtained chinolein by caustic potash distillation of quinine and strychnine. Hofmann [191] showed that leukol and chinolein were identical. The name quinoline or chinoline was gradually adopted thereafter, although "leucoline" still continued to appear in the earlier literature.

[188] Unverdorben, O., *Pogg. Ann.*, **8**, 253–65, 477–87 (1826), **11**, 59–74 (1827).

[189] Anderson, T., *Trans. Roy. Soc. Edinburgh*, **16**, 123–36 (1846); *Edinburgh New Phil. J.*, **41**, 146–56, 291–300 (1846); *Ann.*, **60**, 86–103 (1846). Calm, A., and von Buchka, K. H., *Die Chemie des Pyridines und seiner Derivate*, F. Vieweg und Sohn, Braunschweig, 1891, 633 pp.

[190] Gerhardt, C., *Ann.*, **42**, 310–3 (1842), **44**, 279–80 (1842).

[191] Hofmann, A. W., *Ann.*, **47**, 37–87 (1843), **53**, 427–8 (1845).

[186] Cantrell, T. L., U. S. Pat. 2,195,510 (1940).

[187] Stevens, D. R., and Gruse, W. A., U. S. Pat. 2,265,582 (1941).

Pyridine and the lower-boiling homologs are obtained from coal carbonization products, both at the coke plant, from the ammonia saturator liquor, and from distillates of coal tar. A review of the coke-plant recovery of low-boiling pyridine bases is given by Hill in Chapter 27. The recovery of crude pyridine bases from coal tar is made by sulfuric or sometimes hydrochloric acid extraction of the lowest-boiling distillates which are obtained in the redistillation of crude naphthalene or tar acid oils. Extraction with acids is usually preceded by caustic extraction in order to remove phenols. Sulfuric acid combines with the pyridine bases to form the water-soluble sulfates which are separated from the non-aqueous oils by decantation. The acid-tar base sulfate solution may first be steamed in order to volatilize dissolved oils, or it may be directly neutralized with caustic soda or ammonia whereby crude pyridine bases are regenerated, which, after drying over caustic soda or by distillation with benzene, are ready for purification by fractional distillation.

A good grade of pyridine from coal tar was isolated by Williams [192] in 1855. He obtained the compound by fractional distillation of the crude bases, removal of aniline with nitric acid, and fractional crystallization of the platinum salts of the resultant bases. The fraction boiling at 116° C was considered to be pyridine. This boiling point approximates the best value given for pyridine today.

β-Picoline, the second pyridine homolog in order of ascending boiling point, was first found in coal tar by Mohler [193] in 1888, almost two decades after it had been prepared synthetically. Schulze and Laden-

burg [194] are credited with the first preparation of γ-picoline from coal tar. A considerable number of reports have been published on the isolation of the aforementioned bases as well as on the resolution of tar-base mixtures of the dimethyl- and trimethylpyridines. Heap and others [195] have reported the separation of high-grade pyridine and α-picoline by fractional distillation and subsequent alcohol recrystallization of the zinc chloride salts of these bases. One method of obtaining pure grades of β-picoline, γ-picoline, and 2,6-lutidine from their narrow boiling-range mixture was reported by Lidstone in 1940.[196] His method consisted of recrystallization of the oxalic acid salts of the picolines and of the mercuric chloride salt of lutidine.

In 1942, Cislak and Wheeler [197] patented two processes for the purification of β-picoline. Crude β-picoline was reacted with sulfur or was catalytically oxidized under such conditions that substantially only the contaminants γ-picoline and α,α-lutidine were affected. The unreacted β-picoline was then separated from each of the reaction mixtures by distillation or by aqueous extraction followed by distillation.

Developments in improved fractional-distillation techniques and equipment have permitted direct separation of pyridine and α-picoline from their tar-base mixtures and have obviated the necessity for chemical treatment save where two or more pyridine homologs have approximately the same boiling range.

Just as Kekulé's proposal for the chemical configuration of benzene opened the

[192] Williams, C. G., *Edinburgh New Phil. J.*, 2, 324–31 (1855).

[193] Mohler, J., *Ber.*, 21, 1006–15 (1888).

[194] Schulze, K. E., *Ber.*, 20, 409–14 (1887). Ladenburg, A., *Ann.*, 247, 1–98 (1888). Stoehr, C., *J. prakt. Chem.*, (2), 43, 154–6 (1891).

[195] Heap, J. G., Jones, W. J., and Speakman, J. B., *J. Am. Chem. Soc.*, 43, 1936–40 (1921).

[196] Lidstone, A. G., *J. Chem. Soc.*, 143, 240–3 (1940).

[197] Cislak, F. E., and Wheeler, W. R., U. S. Pats. 2,272,159, 2,300,741 (1942).

door to a logical study of aromatic compounds, the establishment of a trustworthy structure for the pyridine molecule furthered the understanding of heterocyclic compounds. The formula for pyridine, and concurrently for quinoline, was arrived at independently by Körner and Dewar.[198] They agreed that the benzene configuration could be applicable to pyridine by substitution of nitrogen for one of the CH groups in the benzene ring. By analogy, quinoline would then have the same relationship to pyridine as naphthalene has to benzene. The considerations by which this structural formula was evolved were the subject of an interesting review by Dobbin in 1934.[199]

Several methods for the syntheses of pyridine derivatives are of a limited nature or yield complex mixtures of the bases and are costly because of the reagents required. α-Picoline was prepared from the sulfate of the alkaloid sparteine by distillation over zinc dust,[200] and γ-picoline by the thermal rearrangement of pyridine methiodide.[201] β-Picoline was first made by Baeyer [202] in 1870, from acrolein and ammonia. Among the general methods for the synthesis of pyridine homologs is that of Schwartz [203] from glycerin, phosphorus pentoxide, and ammonium phosphate. This method is basically the same as Baeyer's. Another classic procedure is the Hantzsch synthesis,[204] in which the reactants are a β-ketonic ester or diketone and an aldehyde and ammonia. A comprehensive review of

these syntheses has been made by Hollins.[204]

Although numerous references are found on the separation of pyridine and methylpyridines from coal tar, quinoline and its homologs have not received such extensive study. The reasons for this situation are the difficulties of separating the components of a coal-tar quinoline mixture and, more particularly, the discovery of excellent synthetic preparation schemes. One exception to this is the investigation of high-boiling crude coal-tar bases as reported by Jantzen [205] in 1932. His initial crude material had an approximate boiling range from 230 to 265° C and was substantially free of methylated pyridines. After the removal of nonbasic contaminants the material was subjected to a rough fractionation under vacuum. A cut was obtained which contained essentially only quinoline and those bases boiling up to 265° C. The method of separation of the constituents of this cut consisted of thorough fractional distillation and recrystallization of the sulfates of the resultant fractions which contained compounds of approximately the same boiling range. The following table indicates the relative proportions of quinolines and isoquinolines which were found by Jantzen in his high-boiling bases:

	PERCENT
Quinoline	41.03
Isoquinoline	13.02
2-Methylquinoline	10.60
3-Methylquinoline	1.79
4-Methylquinoline	5.70
5-Methylquinoline	0.30
6-Methylquinoline	1.80
7-Methylquinoline	1.35
8-Methylquinoline	1.46
1-Methylisoquinoline	1.04
3-Methylisoquinoline	2.05

198 Körner, W., *Compt. rend.*, **69**, 475–7 (1869) ; *Ber.*, **2**, 219–20 (1869). Dewar, J., *Chem. News*, **23**, 38–41 (1871).

199 Dobbin, L., *J. Chem. Education*, **11**, 596–600 (1934).

200 Ahrens, F. B., *Ber.*, **26**, 3035–42 (1893).

201 Lange, O., *Ber.*, **18**, 3436–41 (1885).

202 Baeyer, A. von, *Ann.*, **155**, 281–311 (1870).

203 Schwartz, P., *Ber.*, **24**, 1676–8 (1891).

204 Hantzsch, A., *Ann.*, **215**, 1–82 (1882). Hollins, C., *Synthesis of Nitrogen Ring Compounds Containing a Single Hetero-Atom (Nitrogen)*, Ernest Benn, London, 1924, 423 pp.

205 Jantzen, E., *Das fraktionierte Distillieren und das fraktionierte Verteilen als Methoden zur Trennung von Stoffgemischen*, Verlag Chemie G.m.b.H., Berlin, 1932, pp. 117–37.

	PERCENT
2,8-Dimethylisoquinoline	0.75
1,3-Dimethylisoquinoline	....
Base $C_{10}H_9N$ (F.P. 85–86°)	0.05
6-Methylisoquinoline ?	....
Base $C_{10}H_9N$ (F.P. 76°)	0.08
Base C_7H_5NS (F.P. 49.50°)	0.10
Thioisoquinoline ?	....

Quinoline was first synthesized by Konigs [206] in 1879 by passing allylaniline over hot lead. The Skraup synthesis [207] of a year later consisted of reacting a primary amine, glycerin, and sulfuric acid and the use of nitrobenzene as an oxidizing agent. This method, with its modifications for methylquinolines by Doebner and Miller,[208] and others, has continued to be useful although a number of ramifications have since been introduced as well as some basically different methods.

At present the separation of quinoline from coal-tar bases has again become competitive to the synthetic Skraup process. Suitable coal-tar distillates, which have an appreciable concentration of oils boiling in the range from 235 to 240° C, are extracted with dilute sulfuric acid. The resultant tar-base sulfates are then alkalized to release the bases from which quinoline is prepared by thorough fractional distillation.

One of the earliest commercial applications of pyridine bases was in the purification of anthracene.[209] A number of present-day methods for the preparation of anthracene from coal tar also require the use of pyridine bases. The pyridine bases have excellent solvent properties for most organic materials but merit a certain un-

popularity because of their noxious odor. A difficulty in their use as solvents has been the frequent failure to recognize the influence of water contamination. In 1909, MacKenzie [210] pointed out that pyridines form a constant-boiling hydrate whose solvent properties are greatly inferior to those of dried pyridines. The disagreeable odor of pyridine bases has accounted for their most important early demands, namely, for the denaturization of alcohol. In 1910, Germany alone used about 1.5 million pounds of pyridine bases for this purpose.[211] This same denaturant, along with methyl alcohol, was formerly important in the United States. The bases used were principally those boiling up to 160° C.

Since 1930 a great deal of new interest has developed in pyridine bases, primarily from the pharmacology standpoint. Since first prepared, by Ewins and Phillips in England, sulfapyridine has been used in every type of infection for which sulfanilamide has been found effective. In many pneumococcal infections it appears to be superior, although further investigations are being pursued to ascertain its position more fully. Uses of sulfapyridine or its sodium salt have been reported in cases of staphylococcal, gonococcal, and streptococcal infections.[212] The extensive application of this drug may be realized from the fact that in 1940 the United States production of sulfapyridine and its sodium salt was over 102,000 pounds.[213]

The nicotinic acid and nicotinamide now popular for food enrichment may be prepared from pyridine, β-picoline, quinoline,

[206] Konigs, W., Ber., 12, 453 (1879).

[207] Skraup, Z. H., Monatsh., 1, 316–8 (1880). Gilman, H., and Blatt, A. H., Organic Syntheses, John Wiley & Sons, New York, 1941, Collective Vol. I, pp. 478–82.

[208] Doebner, O., and Miller, W. v., Ber., 16, 1664–7 (1883).

[209] Chemische Fabrik A.-G., Ger. Pat. 42,053 (1887).

[210] MacKenzie, K. G., Ind. Eng. Chem., 1, 360–2 (1909).

[211] Lunge, G., Vol. II, p. 903, of ref. 59.

[212] Jenkins, G. L., and Hartung, W. H., The Chemistry of Organic Medicinal Products, John Wiley & Sons, New York, 2nd ed., 1941, pp. 424–5.

[213] United States Tariff Commission, Synthetic Organic Chemicals, 1940, pp. 23, 40.

or nicotine. The relation of nicotinic acid to pellagra was reviewed by Elvehjem [214] in 1940. Some of the prophylactic measures taken against this deficiency disease have been in the direction of the fortification of certain foods with nicotinic acid and, particularly, nicotinamide.

In 1935, Binz [215] pointed out the use of certain iodopyridines, specifically, the sodium salt of 5-iodo-2-pyridone-N-acetic acid, as a superior X-ray contrast substance in urology. It was claimed that the human system can safely take much more iodine in this form than in those previously used. Pyridine arsonic acids have in like manner permitted the larger assimilation of arsenicals in therapeutic practice.

Since its successful preparation by Tschitschibabin [216] in 1915, from pyridine and sodamide, 2-aminopyridine has had extensive use in medicine in the preparation of sulfapyridine, 2-pyridyl-N-pyrrole, and other compounds. The primary amino group in this and other aminopyridines may be diazotized and coupled to give dyes.

Hydrogenation of pyridine can be carried out electrolytically to produce hexahydropyridine or piperidine. This compound is a strong base, and from it is made a rubber accelerator, piperidinepentamethylenedithiocarbonate.

Quinoline and its derivatives are of interest to pharmacology if for no other reason than because of their relationship to quinine. A considerable amount of work has been done in the search for anti-malarial substitutes for quinine. Much of this research concerns quinoline and methylquinolines.

214 Elvehjem, C. A., *Physiol. Revs.*, **20**, 249–71 (1940).

215 Binz, A., *Angew. Chem.*, **48**, 425–9 (1935).

216 Tschitschibabin, A. E., and Seide, O., *Chem. Zentr.*, **86**, I, 1004 (1915).

Of the synthetic quinoline derivatives, 8-hydroxyquinoline or chinosol is one of the most widely known. It is used as an antiseptic and as an analytical reagent. Its derivatives are used as iodoform substitutes and as photographic sensitizers. Coupling of hydroxyquinoline can yield azo dyes which have moderate significance. Among other quinoline-derived medicinals are oxyquinoline citrate, sulfate, tannate, and benzoate, and iodoxyquinoline-5-sulfonic acid.

The total United States production of quinoline dyes in 1940, as reported by the Tariff Commission,[213] was 273 pounds. Of these, quinoline yellow is the most important. It is made from methylquinoline and phthalic anhydride and is a commercially important, fast, greenish yellow dye. Some of the most useful photographic sensitizers, the carbocyanines, isocyanines, and cyanines, are synthesized from the quinoline bases.

CARBAZOLE
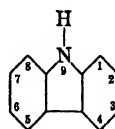
Carbazole
(dibenzopyrrole; diphenyleneimide)

The only coal-tar pyrrole derivative which has attained industrial importance is carbazole. Although compounds of the pyrrole series appear throughout most of the distilling range of coal tar, they have been generally considered but minor impurities occurring along with other coal-tar materials and seldom as specifically separable compounds. Higher-boiling pyrroles such as the indoles or benzopyrroles have been isolated from coal-tar oils but not in sufficient quantities to merit much commercial in-

terest. Kruber has done outstanding work on these compounds.[217]

Carbazole may be considered as the dibenzo homolog of pyrrole. Its name is derived from the fact that, although the compound contains nitrogen, it has somewhat the general characteristics of a hydrocarbon.

Carbazole is found in the crude anthracene fraction of coal tar. It was discovered in 1872 by Gräbe and Glaser [218] incidentally to their purification of anthracene by caustic potash fusion. The alkali melt from their fusion when separated and hydrolyzed yielded crude carbazole. Although some methods for the purification of anthracene have aimed at the elimination of carbazole alone, most procedures try to incorporate the simultaneous isolation of carbazole and anthracene and even to effect some purification of phenanthrene.

Carbazole is the imide of diphenyl. It is a very weak base and has an active hydrogen on the nitrogen atom which is readily displaced by alkali and other groups. These properties plus its solubility characteristics are factors which have been used in separating the compound from coal-tar fractions.

The preparation of carbazole from crude coal-tar anthracene is the subject of numerous reported investigations both academic and patent. A majority of the procedures deal with some ramifications of Gräbe's original caustic fusion process.

Portheim's [219] patent, 50 years after Gräbe, may be cited as an example of this caustic treatment. According to this patent, potassium hydroxide is caused to react with a solvent naphtha solution of a partially purified anthracene cake. Insoluble

potassium carbazolate is precipitated and separated from the hot solution of anthracene and oils, after which carbazole is regenerated by hydrolysis.

Hydrogenation processes are also frequently mentioned. In these methods [94, 220] the crude material is hydrogenated, generally at elevated temperatures and in the presence of catalysts, whereby anthracene and other solid hydrocarbons are converted to liquids from which the unreacted carbazole may be separated by crystallization.

Solvent treatments have been commonly reported for the concentration of carbazole or even for its ultimate purification. The best known of these are recrystallization from pyridine bases in which the carbazole is concentrated in the mother liquor.[221] Other solvent methods include crystallization from tar acids [222] and benzene, acetone, or carbon tetrachloride.[223] Distillation or sublimation of crude anthracene along with solvents is listed among the methods of purifying carbazole. Among them may be mentioned the use of fractions of creosote oil.[224]

A partial concentration of carbazole may be made by reacting crude anthracene with maleic anhydride, whereby the anthracene is removed as an alkali-soluble addition product.[136]

Still other preparation methods depend upon the specific reactivity of the carbazole nitrogen group. Treatments of a crude carbazole concentrate with strong sulfuric acid have been reported in which the impurities are destroyed by sulfonation and

[217] Kruber, O., Ber., 62B, 2877–80 (1929).

[218] Gräbe, C., and Glaser, C., Ber., 5, 12 5 (1872); Ann., 163, 343–60 (1872).

[219] Portheim, E., U. S. Pat. 1,404,055 (1922).

[220] Kosaka, Y., and Kayamori, A., J. Soc. Chem. Ind., Japan, 44, No. 1, Suppl. Binding, 23 (1941); Chem. Abs., 35, 5108 (1941).

[221] Gluzman, L. D., Ukrain. Khem. Zhur., 12, 367–8 (1937).

[222] Leroux, H., U. S. Pat. 1,318,212 (1920).

[223] Thatcher, C. J., U. S. Pat. 1,672,630 (1928).

[224] Kenngott, E., Chem.-Ztg., 56, 969–70 (1932).

carbazole is regenerated upon aqueous dilution.[225] When a lower temperature and solvent dilution are used, an insoluble carbazole sulfate is formed and the anthracene and other impurities are unaffected. Yura and Oda [226] reacted crude anthracene with formaldehyde, alcohol, and sodium bisulfite. The alcohol-soluble N-methylcarbazole was formed which was then separated from the insoluble anthracene and reconverted to carbazole. Carbazole is usually manufactured by the caustic potash processes.

The syntheses of carbazole and its derivatives have been about as numerous as those dealing with its preparation from coal-tar fractions. A brief mention will be made of but a few.

The earliest procedure was discovered by Gräbe [227] at about the same time that he found carbazole in crude coal-tar anthracene. He pyrolyzed aniline and diphenylamine by passing them through a hot tube. The yields of carbazole were very poor. Most of the subsequent syntheses have also been of a pyrolytic nature. The use of various catalysts has greatly increased the carbazole yields from the above-mentioned starting materials. Zelinsky and others [228] claimed to have obtained good yields of carbazole by pyrogenesis of Gräbe's initial materials at a temperature of near 300° C and in the presence of a dehydrogenating catalyst such as platinum and charcoal. Morgan and Walls [229] prepared carbazole by the pyrolysis of o-xenylamine along with an oxidation catalyst. In 1891, Täuber [230] effected a quantitative formation of carbazole by heating 2,2'-diaminodiphenyl

with its hydrochloride. He also introduced a later modification which consisted of tetraäzotizing this diamine and then reacting it with potassium sulfide.

The principal use of carbazole is in the preparation of Hydron Blue dyes. They comprise a series of blue vat dyes which have to some extent displaced Indigo and Indanthrene dyes because of their superior fastness. Hydron Blue R is prepared by condensing p-nitrosophenol with carbazole in the presence of sulfuric acid and reacting the resultant ice-precipitated solid with an alkali polysulfide. A blue vat dye results. If the last reaction is carried out with an excess of sulfur, blue dyes are formed which are easily soluble in alkaline hydrosulfide and are therefore used as vat dyes and not as sulfur colors. Among other carbazole dyes are Hydron Blue G which is formed from N-ethylcarbazole instead of carbazole, Hydron Yellow G from N-ethylcarbazole and phthalic anhydride, and Carbazole Yellow from diazotized diaminocarbazole coupled with salicylic acid.

In 1937, Armour and Company patented processes for the Friedel-Crafts synthesis of various carbazole alkyl ketones by condensing carbazole and certain long-chained aliphatic acid chlorides. The resultant products such as 2-stearylcarbazole and 2,8-dilaurylcarbazole have been suggested as being useful in electrical insulations, as waxing and polishing compounds, and for addition to lubricating oils.[231]

Marqueyrol reported a study in 1928 on the use of carbazole as a stabilizer for smokeless powder.[232]

Production of resins from carbazole and olefins is the subject of several recent patents. One, in 1933, deals with the prepa-

225 Weiss, J. M., U. S. Pat. 1,301,796 (1919).
226 Yura, S., and Oda, R., J. Soc. Chem. Ind. Japan, 43, Suppl. Binding, 392-3 (1940).
227 Gräbe, C., Ann., 167, 125-30 (1873).
228 Zelinsky, N. D., Titz, I., and Gaverdovskaya, M., Ber., 59B, 2590-3 (1926).
229 Morgan, G. T., and Walls, L. P., J. Soc. Chem. Ind., 57, 358-360 (1938).
230 Täuber, E., Ber., 24, 197-201 (1891).

231 Ralston, A. W., and Christensen, C. W., U. S. Pat. 2,101,559 (1937).
232 Marqueyrol, M., Mém. poudres, 23, 158-77 (1928).

ration of a soft resinous product from propene and carbazole in the presence of a hydrosilicate material.[233] More interesting resins appear to be those obtained from N-vinylcarbazole, which has been reported in a number of patents to the I. G. Farbenindustrie Aktiengesellschaft. One of these deals with the reaction of carbazole with vinyl chloride to form N-vinylcarbazole, which, by polymerization, is claimed to give resins possessing unusual properties.[234]

COMPOUNDS FROM THE CARBONIZATION OF COAL
With
SUSAN E. WOOLRIDGE

Many lists of compounds reported found in coal tar have been published, among

them one by Fisher in 1938.[235] A new list is given in Table XIX, where the compounds identified from the low- and high-temperature carbonization of coal are arranged in order of ascending boiling points at normal atmospheric pressure. Both mercury [236] and germanium [237] have also been reported present in coal tar, and traces of other elements have been found, mostly in pitch coke.[238]

[233] Michel, R., U. S. Pat. 1,916,629 (1933).

[234] Reppe, W., and Keyssner, E., U. S. Pat. 2,066,160 (1936). Keyssner, E., and Wolff, W., U. S. Pats. 2,123,733–4 (1938). Reppe, W., Keyssner, E., and Nicolai, F., U. S. Pat. 2,153,993 (1939). Dykstra, H. B., and Jacobson, R. A., U. S. Pat 2,238,682 (1941).

[235] Fisher, C. H., *U. S. Bur. Mines, Bull.* **412** (1938), 70 pp.

[236] Aston, F. W., *Nature*, **119**, 489 (1927). Kirby, W., *J. Soc. Chem. Ind.*, **46**, 422 (1927).

[237] Goldschmidt, V. M., *Nachr. Ges. Wiss. Gottingen, Math.-physik. Klasse*, **1930**, 1–4. Kostrikin, V. M., *J. Applied Chem. (U.S.S.R.)*, **12**, 1449–54 (1939).

[238] Churchill, H. V., private communication, April 1, 1932. Demann, W., *Tech. Mitt. Krupp*, **4**, 1–7 (1936).

TABLE XIX

COMPOUNDS IDENTIFIED FROM THE CARBONIZATION OF COAL

(The first reference given is that of the boiling point and may or may not refer to coal tar. The H or L after the melting point indicates when the compound has been identified only from high- or from low-temperature carbonization; otherwise it has been found in both. d. = decomposes. s. = sublimes.)

No.	Compound	Formula	Boiling Point	Melting Point	H	L	References
1.	Hydrogen	H_2	$-252.5°$				239; 240-2
2.	Nitrogen	N_2	$-194°$				239; 240-2
3.	Carbon monoxide	CO	$-190°$				239; 240-1, 243
4.	Oxygen	O_2	$-183°$		H		244; 240
5.	Methane	CH_4	$-161.7°$				245; 240, 246 7
6.	Ethylene	C_2H_4	$-103.7°$				248, 240, 247, 249–50
7.	Ethane	C_2H_6	$-88.6°$				245; 240, 246-7

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* TABLE XIX—*Continued*

Compounds Identified from the Carbonization of Coal

No.	Compound	Formula	Boiling Point	Melting Point	H–L	References
8.	Hydrogen chloride	HCl	−83.7°	.....		244; 241, 251–2
9.	Acetylene	C_2H_2	−82°	. ...		244; 240, 253
10.	Carbon dioxide	CO_2	−80°	.....		239; 240–1, 243
11.	Hydrogen sulfide	H_2S	−61.8°	.....		244; 243, 253–6
12.	Propylene	C_3H_6	−47.6°	.....		257; 240, 249–50
13.	Propane	C_3H_8	−42.2°	.....		245; 246–7
14.	Allene	C_3N_4	−34.3°	−136.1°	H	258; 259
15.	Ammonia	NH_3	−34°	.....		239; 241, 247, 260
16.	Allylene (methylacetylene)	C_3H_4	−23.5°	.....		246; 261
17.	Cyanogen	C_2N_2	−20.5°	.....		244; 242, 262–3
18.	Sulfur dioxide	SO_2	−10.0°	.....	H	244; 247
19.	Butene-1	C_4H_8	−6.1°	.....		264; 243, 249–50, 265
20.	1,3-Butadiene	C_4H_6	−4.5°	−108.7°		266; 243, 249–50, 259, 260
21.	n-Butane	C_4H_{10}	−0.5°	.....		267; 247, 249, 268
22.	Butene-2	C_4H_8	+1.0°	.....	L	264; 249
23.	Methylmercaptan	CH_4S	6°	.....		269; 249, 270–2
24.	Ethylacetylene	C_4H_6	18°	.....	H	261
25.	1-Methylallene	C_4H_6	18°	.....	H	259
26.	Acetaldehyde	C_2H_4O	20.2°	−123.45°	L	273; 249, 254, 272, 274–5
27.	Hydrogen cyanide	HCN	26°	−14°		239; 241–2, 276
28.	Crotonylene (dimethylacetylene)	C_4H_6	27.1°	.....	H	264; 243, 261, 270
29.	Methylbutane	C_5H_{12}	27.9°	.....	L	267; 247, 249
30.	Isopropylacetylene	C_5H_8	28°	.....	H	261
31.	2-Methylbutadiene	C_5H_8	ca. 35°	.....	H	259
32.	n-Pentane	C_5H_{12}	36.1°	.....		267; 243, 247, 249, 268, 270, 277
33.	Pentene-2	C_5H_{10}	36.3°	. ...	L	278; 239
34.	Ethylmercaptan	C_3H_6S	37°	. ...	H	260; 269, 271, 279
35.	Dimethylsulfide	C_2H_6S	37.5°	. ...		269; 249, 271 2

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TABLE XIX—*Continued*

COMPOUNDS IDENTIFIED FROM THE CARBONIZATION OF COAL

No.	Compound	Formula	Boiling Point	Melting Point	H-L	References
36.	Isobutylacetylene	C_6H_{10}	39°	.....	H	261
37.	Pentene-1	C_5H_{10}	40°	.....		280; 243, 247, 249, 270
38.	Cyclopentadiene	C_5H_6	41°	.....		260; 243, 249, 281-2
39.	1,1-Dimethylallene	C_5H_8	41°	.....	H	259
40.	Valylene (1,4-pentadiene)	C_5H_8	41-42°	.....	H	247; 283
41.	1-Methylbutadiene	C_5H_8	42°	.....	H	259
42.	Carbon disulfide	CS_2	47°	.. ..		260; 249, 270, 272, 284-5
43.	Propylacetylene	C_5H_8	48-49°	.....	H	261
44.	Ammonium sulfide	$(NH_4)_2S$	d. ca. 50°	.....	H	273; 260
45.	Methylethylacetylene	C_5H_8	55-56°	.....	H	261
46.	Diethylamine	$C_4H_{11}N$	55.5°	.....	L	244; 254
47.	Acetone	C_3H_6O	56°	.....		260; 249, 272, 274-5, 286-90
48.	Ammonium carbonate	$(NH_4)_2CO_3$	d. 58°	.....	H	244; 260
49.	Methylisocyanide	C_2H_3N	59.6°	.....	H	82; 291
50.	Ammonium cyanate	NH_4CNO	d. 60°	.. ..	H	244; 260
51.	2-Methylpentane	C_6H_{14}	62°	.....	L	239; 249
52.	2-Methyl-2,3-pentene	C_6H_{12}	62.5-64°	.....	L	239
53.	Methyl alcohol	CH_4O	63°	.. ..	L	273; 274
54.	3-Methylpentane	C_6H_{14}	63.3°	.. ..	L	267; 292
55.	Hexene-2	C_6H_{12}	64°	....	L	239
56.	n-Hexane	C_6H_{14}	68.8°	.....		293; 243, 249, 268, 277
57.	Hexene	C_6H_{12}	69°	.....		260; 247, 282, 294
58.	2,3-Dimethylbutadiene	C_6H_{10}	69°	.....	H	259
59.	Diethylacetylene	C_6H_{10}	ca. 70°	.....	H	261
60.	Butylacetylene	C_6H_{10}	71°	.....	H	295; 261
61.	Heptane	C_7H_{16}	77-79°	.....	L	202; 239
62.	Ethyl alcohol	C_2H_6O	78.37°	.....	H	273; 296
63.	Methyl ethyl ketone	C_4H_8O	80°	.. ..		260; 249, 272, 274-5, 287, 289
64.	Benzene	C_6H_6	80.09°	5.51°		297; 61-2, 210, 243, 260, 275, 284, 290, 298, 299-304
65.	Cyclohexane (hexahydrobenzene)	C_6H_{12}	80.8°	.....	H	305; 304, 306

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TABLE XIX—*Continued*

COMPOUNDS IDENTIFIED FROM THE CARBONIZATION OF COAL

No.	Compound	Formula	Boiling Point	Melting Point	H-L	References
66.	Methyl cyanide (acetonitrile)	C_2H_3N	81.6°	41°		239; 249, 260, 272, 275, 285
67.	Tetrahydrobenzene (cyclohexene)	C_6H_{10}	83.1°	. . .	H	307; 247, 282
68.	Thiophene	C_4H_4S	84°	. . . . .	H	260; 243, 282, 308–9
69.	Dihydrobenzene	C_6H_8	84°	. . . .	H	260; 247, 282
70.	Methylpropylacetylene (4-hexyne)	C_6H_{10}	84°	.	H	261
71.	Triethylamine	$C_6H_{15}N$	89.5°	. . .	L	244; 254
72.	Diethyl sulfide	$C_4H_{10}S$	92°	. .	H	269; 271, 310
73.	Heptene	C_7H_{14}	98°	. . .	H	260; 247, 282
74.	*n*-Heptane	C_7H_{16}	98.4°	. . .		258; 249, 268, 269, 277, 292, 311–2
75.	Ethyl propionate	$C_5H_{10}O_2$	99.1°	−73.9°	L	273; 287
76.	Water	H_2O	100°	0°		239; 240–1, 243
77.	Formic acid	CH_2O_2	100.7°	8.4°	L	273; 254, 313–4
78.	Methylcyclohexane (hexahydro-toluene)	C_7H_{14}	101.2°	. . . . .		305; 249, 315
79.	Methyl *n*-propyl ketone	$C_5H_{10}O$	102.3°	−77.8°	L	316; 287
80.	Toluene	C_7H_8	110.8°	. . . . .		305; 62, 243, 252, 255, 275, 290, 292, 299, 303, 317 8
81.	2-Methylthiophene (thiotolene)	C_5H_6S	112–113°	. . . . .	H	304; 269, 319–20
82.	3-Methylthiophene	C_5H_6S	114°	. . .	H	304; 269, 319–20
83.	Pyridine	C_5H_5N	115°	−42°		260; 192, 210, 243, 246 7, 254, 268, 289, 321–33
84.	Acetic acid	$C_2H_4O_2$	119°	16°		82; 254–5, 313–4
85.	Octane	C_8H_{18}	119–120°	. . . .		247; 268, 277
86.	1,4-Dimethylcyclohexane	C_8H_{16}	119–125°	. . . . .	L	316; 315
87.	1,3-Dimethylcyclohexane	C_8H_{16}	120- 125°	. . . .	L	316; 315
88.	Octene	C_8H_{16}	122 125°	−104°	L	316; 292, 312, 315
89.	Paraldehyde	$C_6H_{12}O_3$	124°	. . . . .	L	272
90.	*n*-Octane	C_8H_{18}	125.6°	. . . . .		293; 243, 247, 249, 269, 277, 292, 312

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TABLE XIX—*Continued*

COMPOUNDS IDENTIFIED FROM THE CARBONIZATION OF COAL

No.	Compound	Formula	Boiling Point	Melting Point	H-L	References
91.	α-Picoline (2-methylpyridine)	C_6H_7N	129°	−69.9°		260; 210, 246–7, 268, 323, 325–6, 328–31, 333–7
92.	Azulene	$C_{15}H_{18}$	130° (12 mm.)	.....	L	338; 339
93.	Pyrrole	C_4H_5N	131°	.....	H	260; 161, 304, 324
94.	Dihydroxylene	C_8H_{12}	135°	.....	L	340; 247, 341
95.	Hexahydromesitylene	C_9H_{18}	135–137°	.....	L	342
96.	Ethylbenzene	C_8H_{10}	136.15°	.....	H	305; 243, 343–4
97.	Dimethylthiophene (thioxene)	C_6H_8S	137°	.....	H	260; 345–6
98.	m-Xylene	C_8H_{10}	139.3°	.....		293; 243, 275, 347–8
99.	p-Xylene	C_8H_{10}	139.4°	.....		293; 275, 348–51
100.	1,2,4-Trimethylcyclohexane	C_9H_{18}	141.2°	−86.4°		352; 315, 353
101.	Propionic acid	$C_3H_6O_2$	141.35°	−20.8		273; 313–4, 354
102.	o-Xylene	C_8H_{10}	144°	.....		355; 241, 243, 275, 351
103.	β-Picoline (3-methylpyridine)	C_6H_7N	144.0°	−18.3°		196; 193, 210, 246–7, 260, 330, 356–7
104.	2,6-Dimethylpyridine	C_7H_9N	144.4°	−6.0°		196; 195, 289, 326, 328, 330, 357–60
105.	γ-Picoline (4-methylpyridine)	C_6H_7N	144.6°	+3.8°		196; 210, 246–7, 289, 326, 330, 333, 356, 360–1
106.	Styrene	C_8H_8	146°	....	H	260; 243, 362–5
107.	Nonylene	C_9H_{18}	150°	.....	L	366; 292, 312, 315
108.	n-Nonane	C_9H_{20}	150.7°	.....	L	367; 249, 268, 292, 312
109.	Cumene (isopropylbenzene)	C_9H_{12}	153°	....		260; 62, 255, 275, 304, 368–70

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TABLE XIX—*Continued*

COMPOUNDS IDENTIFIED FROM THE CARBONIZATION OF COAL

No.	Compound	Formula	Boiling Point	Melting Point	H–L	References
110.	2,4-Dimethylpyridine	C_7H_9N	157°	.....		260; 195, 289, 321, 326, 328, 330–1, 333, 335, 356, 358–60
111.	Decane	$C_{10}H_{22}$	158–161°	.....		247; 268, 292
112.	2,5-Dimethylpyridine	C_7H_9N	159.5°	.....		340; 269, 358–60, 371–2
113.	n-Propylbenzene	C_9H_{12}	159.5°	.....	H	293; 304, 373
114.	m-Ethyltoluene	C_9H_{12}	162°	.....	H	260; 243, 269, 373
115.	p-Ethyltoluene	C_9H_{12}	162°	.....	H	260; 243, 373
116.	2,3-Dimethylpyridine	C_7H_9N	162–163°	.....	H	247; 269, 310
117.	Trimethylthiophene	$C_7H_{10}S$	163°	.....	H	247; 304, 374
118.	3,4-Dimethylpyridine	C_7H_9N	163.5–164.5°	.....		247; 268, 329, 331, 375
119.	n-Butyric acid	$C_4H_8O_2$	164.5°	−5.50°	L	273; 313–4
120.	Mesitylene (1,3,5-trimethylbenzene)	C_9H_{12}	164.6°	.....		376; 241, 243, 275, 289, 315, 377–9
121.	o-Ethyltoluene	C_9H_{12}	164.9°	.....	H	381; 243, 260, 304, 373
122.	4-Ethylpyridine	C_7H_9N	165°	.....	H	82; 382–3
123.	Dihydromesitylene	C_9H_{14}	166–168°	.....	L	341
124.	2,4,5-Trimethylpyridine	$C_8H_{11}N$	167°	.....		260; 360, 375
125.	2,3,4-Trimethylpyridine	$C_8H_{11}N$	168°	.....		269; 358, 382
126.	Pseudocumene (1,2,4-trimethylbenzene)	C_9H_{12}	169.18°	.....		376; 275, 304, 315, 373, 377, 379–80, 384–7
127.	Thiophenol	C_6H_6S	169.5°	.....	H	388; 389
128.	3,5-Dimethylpyridine	C_7H_9N	169.5°	.....		340; 360, 371–2, 382
129.	Dicyclopentadiene	$C_{10}H_{12}$	170°	33°	H	260; 247, 281–2, 390
130.	2,4,6-Trimethylpyridine	$C_8H_{11}N$	171°	.....		260; 193, 246, 268, 321, 324, 328, 329, 331, 335, 358, 360, 382
131.	Decene	$C_{10}H_{20}$	172°	.....	L	366; 312
132.	Hexahydrodurene (1,2,4,5-tetramethylcyclohexane)	$C_{10}H_{20}$	172–174°	.....	L	391
133.	2,3,6-Trimethylpyridine	$C_8H_{11}N$	173–174°	.....		382; 269, 358, 360
134.	Coumarone	C_8H_6O	173–175°	.....		273; 62, 386, 392–4
135.	n-Decane	$C_{10}H_{22}$	174°	.....	L	367; 243, 249, 312, 373, 395

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TABLE XIX—*Continued*

COMPOUNDS IDENTIFIED FROM THE CARBONIZATION OF COAL

No.	Compound	Formula	Boiling Point	Melting Point	H–L	References
136.	Hexahydro-*p*-cresol	$C_7H_{14}O$	174°	.....	L	396
137.	Hemimellitene (1,2,3-Trimethyl-benzene)	C_9H_{12}	176.1°	.	.	376; 304, 380, 386, 397
138.	Cymene (*p*-methylisopropylbenzene)	$C_{10}H_{14}$	177°	.....	H	304; 255, 398
139.	Hydrindene	C_9H_{10}	178°	.....		399; 241, 281, 386, 400–1
140.	Dihydroprehnitene (dihydro-1,2,3,4-tetramethylbenzene)	$C_{10}H_{16}$	180–182°	.....	L	341
141.	Phenol	C_6H_6O	181°	41°		260; 62, 161–2, 177, 254, 256, 274–5, 290, 331, 402–8
142.	Indene	C_9H_8	182°	−2°		399; 62, 243, 386, 409–13
143.	Tetramethylthiophene	$C_8H_{12}S$	183°	.....	L	340; 414
144.	Aniline	C_6H_7N	184°	−6°		260; 161, 191, 329–31, 335, 358, 415
145.	*n*-Valeric acid	$C_5H_{10}O_2$	186.35°	−35.4	L	273; 313–4
146.	2,3,5-Trimethylpyridine	$C_8H_{11}N$	186.75°	.....	L	360; 358
147.	3,4-Dimethylethylbenzene	$C_{10}H_{14}$	189°	.....		380; 386, 397
148.	Pentamethylcyclohexane	$C_{11}H_{22}$	189–191°	.....	L	391
149.	Oxalic acid	$C_2H_2O_4$	d. 189.5°	.....	L	273; 313–4
150.	Ammonium thiocyanate	NH_4SCN	d. 190°	149.6°	H	416; 242
151.	1,3-Dimethyl-5-ethylbenzene	$C_{10}H_{14}$	ca. 190°	.....	L	——; 417
152.	6-Methylcoumarone	C_9H_8O	190–191°	...	H	247; 269, 418
153.	*o*-Cresol	C_7H_8O	191°	31°		260; 168, 169, 177, 254, 256, 268, 289, 325, 331, 402, 405–7, 419–20
154.	Benzonitrile	C_7H_5N	191°	−13°	H	260; 269, 394, 421
155.	Decalin	$C_{10}H_{18}$	191.5–195°	.....	L	386; 387, 422
156.	Undecene	$C_{11}H_{22}$	192°	...	L	366; 312, 414
157.	Methyl heptyl ketone	$C_9H_{18}O$	195°	.....	L	239
158.	Tolylmercaptan	C_7H_8S	ca. 195°	.....	L	244; 275

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TABLE XIX—*Continued*

COMPOUNDS IDENTIFIED FROM THE CARBONIZATION OF COAL

No.	Compound	Formula	Boiling Point	Melting Point	H–L	References
159.	3- or 5-Methylcoumarone	C_9H_8O	195–196°	.....	H	247; 269, 418
160.	*n*-Undecane	$C_{11}H_{24}$	195.8°	.....		367; 239, 247, 249, 268, 312
161.	Durene (1,2,4,5-tetramethyl-benzene)	$C_{10}H_{14}$	196°	.....		424; 275, 289, 380, 386–7, 423
162.	4-Methylcoumarone	C_9H_8O	197–199°	.....	H	247; 269, 418
163.	Isodurene (1,2,3,5-tetramethyl-benzene)	$C_{10}H_{14}$	198°	.....	H	424; 289, 304
164.	1,2-Dimethyl-4-isopropylbenzene	$C_{11}H_{16}$	199°	.....	L	239; 380
165.	*p*-Toluidine	C_7H_9N	200.4°	45°		273; 246, 358, 425
166.	*o*-Toluidine	C_7H_9N	200.7°	−24.4°		273; 246, 425–6
167.	*p*-Cresol	C_7H_8O	201°	36°		260; 169–71, 173, 177, 254, 256, 268, 289, 331, 402, 405–6, 419, 427–9
168.	Acetophenone	C_8H_8O	202°	20°	H	260; 269, 430
169.	*m*-Cresol	C_7H_8O	202°	10.9°		260; 169–71, 173, 177, 254, 256, 268, 269, 274, 289, 325, 331, 402, 405–6, 419–20, 428, 429, 431 2
170.	4-Methylhydrindene	$C_{10}H_{12}$	203°	.....	L	386; 380
171.	1-Methyldecalin	$C_{11}H_{20}$	203–206°	.. ..	L	386; 241, 422
172.	*m*-Toluidine	C_7H_9N	203.3°	.. ..		273; 246, 425
173.	Prehnitene (1,2,3,4-tetramethyl-benzene)	$C_{10}H_{14}$	204.5°	.. ..	L	424; 275
174.	4-Methylindene	$C_{10}H_{10}$	205°	.....		239; 241, 260, 386, 433
175.	*o*-Ethylphenol	$C_8H_{10}O$	206.5–207°	.....	L	434; 177, 405, 429, 435
176.	Tetrahydronaphthalene	$C_{10}H_{12}$	206.8°	.....	H	399; 247, 281, 436
177.	2,4-Xylenol	$C_8H_{10}O$	209°	26°		260; 177, 268, 331, 390, 405–6, 429, 434, 437-8
178.	2,6-Xylenol	$C_8H_{10}O$	211.2°	49°		434; 177, 435
179.	2,5-Xylenol	$C_8H_{10}O$	211.5°	74.5°		434; 177, 268, 331, 390, 405, 429, 437
180.	2,4-Xylidine	$C_8H_{11}N$	212°	.....	H	273; 425
181.	Dodecene	$C_{12}H_{24}$	213°	.. .	L	307; 312
182.	*m*-Ethylphenol	$C_8H_{10}O$	214°	52°		434; 177, 405, 439
183.	2,5-Xylidine	$C_8H_{11}N$	215°	.....	H	273; 425
184.	*n*-Dodecane	$C_{12}H_{26}$	216.2°	.. ..	L	367; 247, 249, 268, 312
185.	1,6-Dimethyldecalin	$C_{12}H_{22}$	217–223.5°	.. ..	L	386; 241, 422
186.	*p*-Ethylphenol	$C_8H_{10}O$	218°	45°		260; 177, 405, 435, 439

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TABLE XIX—*Continued*

COMPOUNDS IDENTIFIED FROM THE CARBONIZATION OF COAL

No.	Compound	Formula	Boiling Point	Melting Point	H–L	References
187.	Naphthalene	$C_{10}H_8$	218°	80°		260; 62, 68–70, 72, 254, 268, 338, 387, 440–50
188.	2,3-Xylenol	$C_8H_{10}O$	218°	73–75°		434; 177, 405, 439
189.	3,5-Xylenol	$C_8H_{10}O$	219.5°	68°		434; 176–8, 268, 289, 331, 335, 390, 405, 435, 439, 451
190.	Mesitol	$C_9H_{12}O$	219.5°	68–69°	L	434; 435, 452
191.	3,5-Xylidine	$C_8H_{11}N$	220–221°	. .	H	273; 425
192.	3,6-Dimethylcoumarone	$C_{10}H_{10}O$	220–222°	. . . . .	H	453
193.	4,5-Dimethylcoumarone	$C_{10}H_{10}O$	220–222°	. . . . .	H	453
194.	4,6-Dimethylcoumarone	$C_{10}H_{10}O$	220–222°	. . . . .	H	418; 453
195.	*p*-Methyl tolyl ketone	$C_9H_{10}O$	222°	. . . .	L	239
196.	Thionaphthene	C_8H_6S	222°	32°	H	260; 243, 454
197.	2,3-Xylidine	$C_8H_{11}N$	223°	. . .	H	273; 425
198.	3,4-Xylenol	$C_8H_{10}O$	225°	65°		260; 177, 268, 289, 331, 405–6, 434–5, 455
199.	Dimethylindene	$C_{11}H_{12}$	225–230°	. . . .		386; 241, 433, 456
200.	4,6-Dimethylhydrindene	$C_{11}H_{14}$	226–232°	. . . .	L	386; 241
201.	Perhydrofluorene	$C_{13}H_{22}$	230°	. . .	L	387
202.	Pseudocumenol (2,4,5-trimethyl-phenol)	$C_9H_{12}O$	232°	71°		316; 390, 429
203.	3-Ethyl-5-methylphenol	$C_9H_{12}O$	232.5–234.5°	55°		439; 452
204.	2,3,4,5-Tetramethylpyridine	$C_9H_{13}N$	233°	. . .		260; 321, 358
205.	Isopseudocumenol (2,3,5-tri-methylphenol)	$C_9H_{12}O$	233°	96°	H	260; 439
206.	Methylnonylcarbinol	$C_{11}H_{24}O$	234–236°	. . . .	L	414
207.	Perhydrodiphenyl	$C_{12}H_{22}$	234–236°	. . . . .	L	387
208.	Perhydroacenaphthene	$C_{12}H_{20}$	235–236°	. . . . .	L	387
209.	Quinoline (leucoline)	C_9H_7N	238°	−15°		260; 161, 191, 205, 268–9, 324, 331, 335, 404, 457–63
210.	Isohomocatechol (1-methyl 2,3-dihydroxybenzene)	$C_7H_8O_2$	d. 239°	47°	L	340; 313, 315
211.	7-Hydroxycoumarone	$C_8H_6O_2$	240°	43°	H	464

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TABLE XIX—*Continued*

COMPOUNDS IDENTIFIED FROM THE CARBONIZATION OF COAL

No.	Compound	Formula	Boiling Point	Melting Point	H–L	References
212.	Methylthionaphthene	C_9H_8S	240–245°	.....	H	465
213.	Hexahydrofluorene	$C_{13}H_{16}$	240–250°	.....	L	466; 467
214.	2-Methylnaphthalene	$C_{11}H_{10}$	241.14°	34.44°		102; 62, 97, 99, 101, 254, 315, 325, 386–7, 468–9
215.	Isoquinoline	C_9H_7N	243.25°	28°		205; 243, 260, 269, 324, 404, 470–1
216.	1-Methylnaphthalene	$C_{11}H_{10}$	244.78°	−30.9°		102; 62, 97, 101, 254, 315, 338, 387, 468–9
217.	4-Hydroxyhydrindene	$C_9H_{10}O$	245°	50°	H	472; 464
218.	Catechol	$C_6H_6O_2$	245°	105°	L	273; 254, 313–4, 419, 434, 473–6
219.	2-Methylquinoline	$C_{10}H_9N$	247.60°	−2°		205; 268, 331, 335, 458
220.	8-Methylquinoline	$C_{10}H_9N$	247.75°	.....	H	205
221.	3,4,5-Trimethylphenol	$C_9H_{12}O$	248°	106°	H	472
222.	Durenol (2,3,5,6-tetramethyl phenol)	$C_{10}H_{14}O$	248°	119°	H	260; 439, 477
223.	Benzoic acid	$C_7H_6O_2$	249°	121°	H	82; 354, 478
224.	Guaiacol (*o*-methoxyphenol)	$C_7H_8O_2$	250°	28°	L	479; 480
225.	Homocatechol (1-methyl-3,4-hy-droxybenzene)	$C_7H_8O_2$	251°	65°	L	273; 313, 315
226.	5-Hydroxyhydrindene	$C_9H_{10}O$	251°	.....	H	472
227.	2-Ethylnaphthalene	$C_{12}H_{12}$	252°	−7.5°		481; 254
228.	1-Ethylnaphthalene	$C_{12}H_{12}$	252.0°	−15.0°	L	481; 254
229.	3-Methylisoquinoline •	$C_{10}H_9N$	252.25°	64.7°	H	205
230.	Indole	C_8H_7N	253°	52.5°	H	260; 442, 477, 482
231.	Dimethylcatechol	$C_8H_{10}O_2$	253°	.....	L	483; 484
232.	Diphenyl	$C_{12}H_{10}$	255.2°	71°		485; 260, 325, 436, 486–8
233.	1-Methylisoquinoline	$C_{10}H_9N$	255.25°	10.1°	H	205
234.	2,8-Dimethylquinoline	$C_{11}H_{11}N$	255.25°	23.2°	H	205
235.	7-Methylquinoline	$C_{10}H_9N$	257.60°	39°	H	205
236.	6-Methylquinoline	$C_{10}H_9N$	258.60° ca.	−22°	H	205

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TABLE XIX—*Continued*

COMPOUNDS IDENTIFIED FROM THE CARBONIZATION OF COAL

No.	Compound	Formula	Boiling Point	Melting Point	H–L	References
237.	o-Methylbenzoic acid	$C_8H_8O_2$	259.2°	103.7°	L	244; 414
238.	3-Methylquinoline	$C_{10}H_9N$	259.55°	16–17°	H	205
239.	2,6-Dimethylnaphthalene	$C_{12}H_{12}$	260.5°	110°		489; 304, 325, 487, 490
240.	2,7-Dimethylnaphthalene	$C_{12}H_{12}$	262°	97°	H	489; 304, 490
241.	1,7-Dimethylnaphthalene	$C_{12}H_{12}$	262°	.....	H	491
242.	1,3-Dimethylisoquinoline	$C_{11}H_{11}N$	262.40°	29.8–30°	H	205
243.	1,6-Dimethylnaphthalene	$C_{12}H_{12}$	262.5°	.....		489; 247, 254, 387, 490
244.	5-Methylquinoline	$C_{10}H_9N$	262.70°	19°	H	205
245.	4-Methylquinoline	$C_{10}H_9N$	264.20°	9–10°	H	205; 247, 254, 304, 492
246.	5- or 7-Methylisoquinoline (probable)	$C_{10}H_9N$	264.90°	76°	H	205
247.	3-Methylindole (skatole)	C_9H_9N	265°	95°	H	260; 217, 493–4
248.	1,5-Dimethylnaphthalene	$C_{12}H_{12}$	265–265.5°	80–80.5°	H	495
249.	6-Methylisoquinoline (probable)	$C_{10}H_9N$	265.50°	85–86°	H	205
250.	7-Methylindole	C_9H_9N	266°	85°	H	260; 217, 493
251.	2,3-Dimethylnaphthalene	$C_{12}H_{12}$	266°	104.5°	H	489; 496 7
252.	1,2-Dimethylnaphthalene	$C_{12}H_{12}$	266–267°	−3.5°	H	498; 491
253.	4-Methylindole	C_9H_9N	267°	5°	H	260; 217
254.	5-Methylindole	C_9H_9N	267°	60°	H	260; 217, 493
255.	3-Methyldiphenyl	$C_{13}H_{12}$	269°	.....	H	260; 499
256.	5,8-Dimethylquinoline	$C_{11}H_{11}N$	>270°	.....	H	500
257.	4-Methyldiphenyl	$C_{13}H_{12}$	271°	48°	H	260; 499
258.	2-Methylindole	C_9H_9N	271–272°	61°	H	493; 494, 501
259.	o-Phenylphenol	$C_{12}H_{10}O$	275°	67.5	H	316; 390
260.	Resorcinol	$C_6H_6O_2$	276.5°	111.6°	L	273; 313, 315, 473
261.	1,3,7-Trimethylnaphthalene	$C_{13}H_{14}$	280°	13.5°	H	502; 503
262.	α-Naphthol	$C_{10}H_8O$	280°	94°		260; 434, 475, 504
263.	Acenaphthene	$C_{12}H_{10}$	280.7°	96°		501; 62, 111, 239, 241, 260, 325, 387, 404, 442, 450, 492, 499, 505–8
264.	α-Naphthofurane	$C_{12}H_8O$	282 284°	....	H	247; 509
265.	β-Naphthofurane	$C_{12}H_8O$	284–286°	50–51°	H	247; 269, 509
266.	2,3,5-Trimethylnaphthalene	$C_{13}H_{14}$	285°	25.3°	H	510
267.	Hydroquinone	$C_6H_6O_2$	285°	172.3°	L	273; 313, 315
268.	2,3,6-Trimethylnaphthalene	$C_{13}H_{14}$	286.0°	102.0°	H	511; 512

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TABLE XIX—*Continued*

Compounds Identified from the Carbonization of Coal

No.	Compound	Formula	Boiling Point	Melting Point	H–L	References
269.	β-Naphthol	$C_{10}H_8O$	286°	123°		260; 434, 473, 475, 504, 513
270.	Diphenylene oxide	$C_{12}H_8O$	287°	86°	H	260; 122, 269, 499, 507, 514–5
271.	2,4,6,-Trimethylquinoline	$C_{12}H_{13}N$	288°	50°	H	494
272.	3,4′-Dimethyldiphenyl	$C_{14}H_{14}$	289°	14°	H	260; 499
273.	4,4′-Dimethyldiphenyl	$C_{14}H_{14}$	292°	122°	H	260; 499
274.	γ-Diphenylenemethane	$C_{13}H_{10}$	295°	118°	H	247; 119
275.	4,5-Benzindan	$C_{13}H_{12}$	295°	.....	H	260; 499
276.	1-Naphthonitrile (1-cyano-naphthalene)	$C_{11}H_7N$	297°	34°	H	260; 499, 516
277.	1-Methyldiphenylene oxide	$C_{13}H_{10}O$	298°	45°	H	260; 499
278.	Fluorene	$C_{13}H_{10}$	298°	115°	H	125; 62, 122, 325, 363, 404, 442, 450, 499, 507, 517–20
279.	Hydroacridine	$C_{13}H_{11}N$	d. 300°	107°	H	521; 281, 522
280.	1-Naphthylamine	$C_{10}H_9N$	301°	.. .	H	523
281.	2-Methyldiphenylene oxide	$C_{13}H_{10}O$	303–304°	66°	H	516
282.	2-Naphthonitrile (2-cyano-naphthalene)	$C_{11}H_7N$	304°	67°	H	260; 499
283.	2-Naphthylamine	$C_{10}H_9N$	306°	.....	H	523; 426
284.	Paraffin (octadecane)	$C_{18}H_{38}$	308°	28.0°		258; 247, 289
285.	Heneicosane	$C_{21}H_{44}$	>310°	40.4°		258; 247, 404
286.	2-Methylfluorene	$C_{14}H_{12}$	318°	104°	H	260; 499
287.	3-Methylfluorene	$C_{14}H_{12}$	318°	85°	H	260; 499
288.	p-Phenylphenol	$C_{12}H_{10}O$	319°	.....	H	524
289.	Melene	$C_{30}H_{60}$	>320°	.	L	525 391, 526
290.	Tricosane	$C_{23}H_{48}$	320.7°	47.4°		258; 247, 404
291.	Tetracosane	$C_{24}H_{50}$	324.1°	51.1°		258; 239, 247, 404, 527
292.	Pentacosane	$C_{25}H_{52}$	>325°	53.3°		247; 239, 404, 527
293.	Docosane	$C_{22}H_{46}$	327°	44.4°		258; 247, 404
294.	Nonadecane	$C_{19}H_{40}$	328°	33°		260; 241, 247, 499
295.	Hexacosane	$C_{26}H_{54}$	>330°	.. .		—; 239, 247, 404, 527
296.	Heptacosane	$C_{27}H_{56}$	>330°	.. .		---; 239, 247, 527
297.	Octacosane	$C_{28}H_{58}$	>330°	. ..		—; 239, 527
298.	Diphenylene sulfide	$C_{12}H_8S$	332°	97°	H	260; 271, 454, 499
299.	Phenanthrene	$C_{14}H_{10}$	340°	100°	H	501; 62, 131–2, 260, 304, 325, 404, 450, 499, 528 9
300.	Tetramethylbiphenol	$C_{16}H_{18}O_2$	341°	.....	H	524
301.	Anthracene	$C_{14}H_{10}$	342.3°	217°		501; 62, 86, 90, 137, 209, 220, 226, 254–5, 303, 315, 325, 338, 450, 499, 505, 530–43

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TABLE XIX—*Continued*

COMPOUNDS IDENTIFIED FROM THE CARBONIZATION OF COAL

No.	Compound	Formula	Boiling Point	Melting Point	H–L	References
302.	Acridine	$C_{13}H_9N$	346°	110°	H	260; 269, 325, 450, 459, 506, 544–6
303.	2-Hydroxybiphenylene oxide	$C_{12}H_8O_2$	348°	143°	H	524
304.	Phenanthridine	$C_{13}H_9N$	349°	106°	H	260; 494, 547
305.	3-Methylphenanthrene	$C_{15}H_{12}$	350°	65°	H	516
306.	Carbazole	$C_{12}H_9N$	352°	244.8°	H	260; 62, 90, 137, 218, 220, 226, 269, 2~0, 325, 404, 450, 539, 548 51
307.	2-Hydroxyfluorene	$C_{13}H_{10}O$	ca. 352°		H	436; 524
308.	4,5-Phenanthrylenemethane	$C_{15}H_{10}$	353°	116°	H	550
309.	9-Methylphenanthrene	$C_{15}H_{12}$	354 355°	92°	H	516
310.	1-Methylphenanthrene	$C_{15}H_{12}$	354–355°	119°	H	516
311.	2-Phenylnaphthalene	$C_{16}H_{12}$	357 358°	103°	H	516
312.	Hydroxyanthracene	$C_{14}H_{10}O$	d. 360°		H	304; 552
313.	Naphthacene	$C_{18}H_{12}$	>360°		H	—; 90, 304, 553
314.	2-Methylanthracene	$C_{15}H_{12}$	>360°	202°		247; 315, 335, 537, 554 5
315.	2,7-Dimethylanthracene	$C_{16}H_{14}$	>360°	241°		— ; 304, 315, 556-7
316.	2,6-Dimethylanthracene	$C_{16}H_{14}$	>360°	250°	L	- , 315, 335, 537, 556
317.	2,3,6-Trimethylanthracene	$C_{17}H_{16}$	>360°	245°	L	—; 315, 537, 558
318.	2,3,6,7-Tetramethylanthracene	$C_{18}H_{18}$	>360°		L	- ; 315, 537
319.	2,6-Dimethylnaphthacene	$C_{20}H_{16}$	>360°	341°	L	335; 537
320.	Nonacosane	$C_{29}H_{60}$	>360°		L	- ; 239, 527
321.	2-Methylcarbazole	$C_{14}H_{11}N$	363°	259°	H	260; 516
322.	1,2,3,4-Tetrahydrofluoranthene	$C_{16}H_{14}$	363 365°	76°		156; 550, 559
323.	Truxene	$(C_9H_6)_2$ or $(C_9H_6)_4$	s. 364 365°	364 65°		560, 269, 413, 561
324.	3-Methylcarbazole	$C_{14}H_{11}N$	365°	207°	H	260; 516

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TABLE XIX—*Continued*

COMPOUNDS IDENTIFIED FROM THE CARBONIZATION OF COAL

No.	Compound	Formula	Boiling Point	Melting Point	H-L	References
325.	Fluoranthene	$C_{16}H_{10}$	382°	109°	H	260; 155, 157, 269, 450, 520, 562-3
326.	2,3,5,6-Dibenzocoumarone	$C_{16}H_{10}O$	392-397°	205°	H	564; 565
327.	Pyrene	$C_{16}H_{10}$	393°	148°	H	260; 156-7, 255, 303, 450, 520, 563, 566-8
328.	1,9-Benzoxanthene	$C_{16}H_{10}O$	395°	.....	H	564
329.	2-Hydroxyphenanthrene (2-phenanthrol)	$C_{14}H_{10}O$	396°	168-69°	H	569
330.	Retene (8-methyl-2-isopropyl-phenanthrene)	$C_{18}H_{18}$	396.8°	.....	H	501; 247, 269, 271, 520
331.	1,2-Benzofluorene (naphtho-fluorene)	$C_{17}H_{12}$	413°	189 90°	H	260; 564
332.	2,3-Benzofluorene (isonaphtho-fluorene)	$C_{17}H_{12}$	415°	208 09°	H	260; 564
333.	Naphtho-2',3'-1,2-anthracene	$C_{22}H_{14}$	>424°	. . ..	H	436; 90
334.	1,2-Benzonaphthacene	$C_{22}H_{14}$	>425°	. .	H	436; 90
335.	Phenanthridone	$C_{13}H_9NO$	435°	293°	H	570
336.	Dibenzothionaphthene	$C_{16}H_{10}S$	ca. 440°	.. .	H	571
337.	Sulfur	S	444.6°	112.8°	H	244; 572
338.	Chrysene	$C_{18}H_{12}$	448.5°	255°	H	501; 144 5, 269, 303, 450, 505, 520, 566, 568, 573-7
339.	Triphenylene	$C_{18}H_{12}$	450°	197°	H	577; 576
340.	2,3-Benzocarbazole (phenyl naphthyl carbazole)	$C_{16}H_{11}N$	ca. 450°	ca. 330°	H	304; 247, 450, 565, 573, 578-81
341.	Crackene	$C_{24}H_{18}$	d. 500°	308°	H	269; 582
342.	Benzerythrene	$C_{24}H_{18}$	>500°	317°	H	—; 583 4
343.	1,2-Benzanthracene	$C_{18}H_{12}$	500-510°	160°	H	573; 304, 577
344.	Perylene	$C_{20}H_{12}$	500-510°	273 74°	H	573
345.	4,5-Benzopyrene	$C_{20}H_{12}$	500 510°	179°	H	573; 436
346.	1,2-Benzopyrene	$C_{20}H_{12}$	500 510°	177°	H	573; 436, 585-6
347.	Picene	$C_{22}H_{14}$	519°	364°	H	587; 243, 304, 520, 588
348.	Ammonium chloride	NH_4Cl	s. 520°	.		244; 241, 251 2, 260, 589

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Dilute ammoniacal liquors are produced in coke and gas plants, and their disposal has been a major problem for these industries since the earliest days. Within the past twenty years great progress in the development of new treatment methods has been made, although the incentive for further improvements has been reduced by the decline in value of the ammonia. In order to facilitate further progress, the technical information on this branch of industrial waste disposal, including composition, quantities, and methods for treatment of the liquors, has been summarized in this chapter.

Twenty years ago the ammoniacal liquors were an important source of ammonia, but the tremendous expansion of the nitrogen-fixation industry has profoundly changed the picture. The price of ammonia has decreased so seriously that in a number of coke plants ammonia is now recovered as sulfate or liquor merely because no cheaper method for its disposal is available. The United States Tariff Commission in 1937 [1] showed that the proportion of the value of the ammonia to the total value of the proc-

essed products per ton of byproduct coke produced declined from 12.1 percent in 1913 to 3.3 percent in 1934. This reduction in value of ammonia stimulated efforts to recover other compounds from the liquors and to develop cheaper and more efficient methods for its disposal.

Another factor has emphasized the need for continued research, that is, the increasing public consciousness regarding the value of our natural resources. This consciousness has led to a steadily rising demand that additional pollution of our rivers and lakes be prohibited, and that existing conditions be improved wherever possible, particularly where wastes with outstandingly objectionable characteristics are discharged into a stream.

In respect to ammoniacal liquors the pollution difficulty has been aggravated by the extremely penetrating medicinal tastes which phenols in solution impart to drinking water after chlorination. As a consequence, a large number of coke plants have avoided discharge of the waste liquors into streams, or have drastically improved the quality. This public pressure has been an important incentive to more intensive study of ammoniacal liquors and their

[1] *U. S. Tariff Comm., Rept.* **114**, Second Series (1937), p. 35.

wastes, and of methods for their treatment. As used in this chapter, phenol is a generic term which includes not only phenol itself but also its higher homologs.

Past investigations have resulted in definite improvements in the situation, so that few coke or gas plants now discharge untreated wastes into streams. Several processes for dephenolizing the liquors have been developed and are in operation at a number of plants, notably the benzol extraction and the Koppers vapor recirculation processes. Both yield a salable product, the return on which materially assists in paying for the cost of treatment.

Biological treatments for purifying the liquor have been investigated, and still waste in admixture with ordinary city sewage has been purified for a number of years in several sewage-disposal plants.

The problem of inorganic salts has been studied, and ammonium chloride of a grade suitable for galvanizing has been produced after evaporating the liquor.

Although these advances have gone far toward improving the situation in many plants, other phases of the problem still require attention. Thus, the low price of ammonia necessitates a search for methods by which its cost of recovery can be reduced. Sulfuric acid is a major item in the cost of ammonium sulfate, and its elimination or methods for reducing its price are receiving attention. Production of ammonium chloride, which is present as such in the liquor, has been restricted by the limited market, but the development of new uses should increase production.

Methods for recovery of the sulfur dioxide in stack gases by use of the liquor have been proposed. The sulfite produced is oxidized to sulfate. Thus, in addition to furnishing the sulfuric acid for combining with the ammonia, such a process has the further advantage that the quantity of sulfur compounds discharged by the plant to the atmosphere is reduced.

Since ammonium bicarbonate has given good results as a fertilizer, its production has received attention in Europe, particularly in Great Britain. In producing this salt, carbon dioxide from the coke-oven gas has been used, as well as that from outside sources.

Ammonia, free or as the chloride, and phenols are the only compounds which have been successfully recovered from ammoniacal liquors to any extent. Attempts to recover other values have been seriously hampered by the high dilution of the compounds. The cost of evaporating the liquor proves a serious item, even where waste heat can be utilized. Concentration of the liquor by recirculation in oven mains has proved practical in a few instances, but the possibilities in using waste heat from other sources should be examined.

Dephenolized waste liquors still contain small amounts of phenol and appreciable concentrations of other organic matter. Although not as objectionable as phenol, organic matter may produce odors, tastes, and color in some streams and may seriously increase the oxygen demand of the water. Few analyses of the organic matter in the liquor have been made, so that little is known about this complex mixture. Increased knowledge should lead to improved methods for elimination of residual compounds, and analytical work is recommended where further purification proves necessary.

The waste liquor from the ammonia stills is used in a number of plants for quenching the incandescent coke from the ovens. This procedure completely eliminates the waste but is open to serious objections from the standpoints of increased

plant corrosion, deleterious effect on coke quality, and possible pollution of surrounding territory with the spray. The substitution of other treatments which will not require evaporation of the waste on the coke but will abate stream pollution should result in considerable savings. Development of the dephenolization processes has been a noteworthy step in this direction.

Although bacterial processes have been used to destroy the organic matter, the action of the organisms is relatively slow, and they may be injured unless the liquor is highly diluted. These factors have resulted in unfavorable costs and high ground area requirements. Methods which will accelerate the action or reduce the degree of dilution required would add to the interest in this method of treatment.

A strictly chemical treatment for eliminating organic matter, such as an oxidation process, should permit a more positive control of purification results. So far, all such processes have proved costly, but they should be reexamined with a view to their utilization for eliminating traces of phenols, as well as for destroying other organic compounds, wherever more complete elimination proves essential.

As the proper solution of a liquor-disposal problem in a particular plant is determined almost exclusively by local conditions, no general statement is possible. An intelligent evaluation of the factors involved will often require a high degree of technical knowledge. A liquor-disposal problem may be studied from three angles: (1) improvement in existing processes for treatment of the liquor and reduction in their costs; (2) development of treatments to eliminate the organic matter, including, if possible, recovery of additional values; and (3) elimination of inorganic matter, particularly recovery of chlorides for sale.

SOURCE OF LIQUORS

The volume of ammoniacal liquor and its composition depend to a large extent on the method of carbonization and on the form in which the ammonia is recovered from the gas. Three methods for recovery of the ammonia, the semi-direct, the indirect, and the direct processes, are in use. In the semi-direct and indirect processes the hot gases from the ovens are cooled, and a large portion of the ammonia is condensed as a dilute, aqueous liquor. In the semi-direct process the ammonia is distilled from this weak liquor and returned to the gas. All the ammonia is finally recovered from the gas as ammonium sulfate. The semi-direct process is used in most American coke plants.

In the indirect process the ammonia remaining in the gas after separation of the condensate is scrubbed out with water. The condensate and scrubber liquors are combined and distilled, and the ammonia may be used for the production of ammonium sulfate, concentrated liquor, or other products. This indirect process is less widely used.

In the direct process, the ammonia is recovered from the gas as ammonium sulfate before the gas is cooled to the point of condensation. The condensate which is produced in subsequent stages of the by-product apparatus, although substantially free from ammonia, will contain some of the organic matter found in the liquors produced by the other processes. Its purification will involve similar treatments. The direct process has been used to some extent in Europe.

Flow sheets for the semi-direct and indirect ammonia-recovery processes are shown in Figs. 1 and 2.
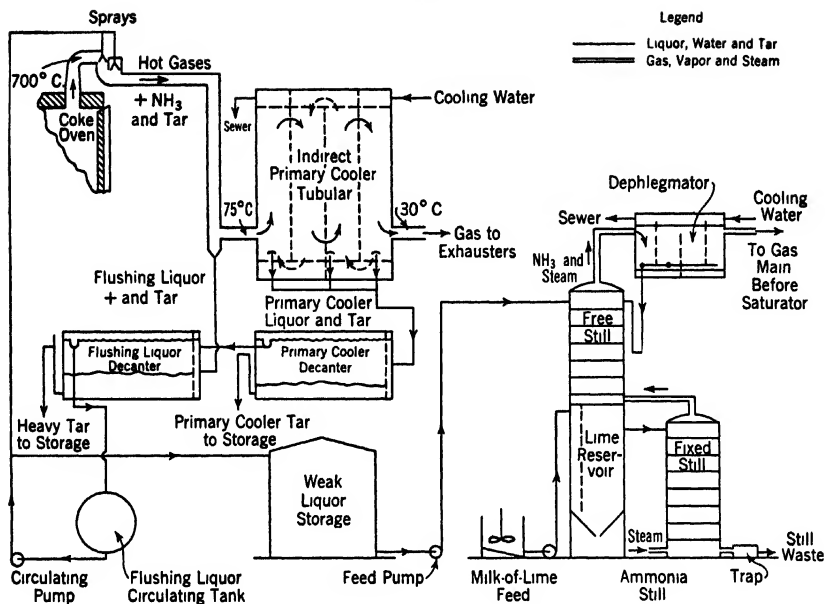
FIG. 1. Flow diagram for production and distillation of weak ammonia liquor in a coke plant using the semi-direct recovery process.

SEMI-DIRECT PROCESS IN BYPRODUCT COKE PLANTS

The hot gases leaving the ovens at a temperature of about 700° C [2] are cooled, first, in the standpipes from the ovens and in the collecting mains and, finally, in the primary cooler. The gas is cooled in the standpipes and mains by direct contact with a large volume of recirculated liquor which is sprayed into the valve box on each standpipe and at points along the mains. The cooling is effected by evaporation of a portion of the water from the liquor. In American practice, the temperature of the gas leaving the mains to enter the primary

cooler varies from 80 to 100° C,[3] and the gas is usually close to saturation with water.

In addition to cooling the gas, the recirculated liquor performs other functions: (1) the larger part of the tar is condensed from the gas; (2) entrained solid and liquid materials are washed out of the gas; (3) ammonium chloride is dissolved from the gas by the liquor; and (4) the large volume of liquor sweeping over the surfaces in the ascension pipes and mains serves to remove pitchy deposits and keep them clean.

Two types of primary coolers are in use, the indirect and the direct type. As its name implies, the indirect type contains tubes through which cooling water is

2 Gluud, W., and Jacobson, D. L., *International Handbook of the By-Product Coke Industry*, Chemical Catalog Co., New York, 1932, p. 460.

3 *Ibid.*, p. 464.
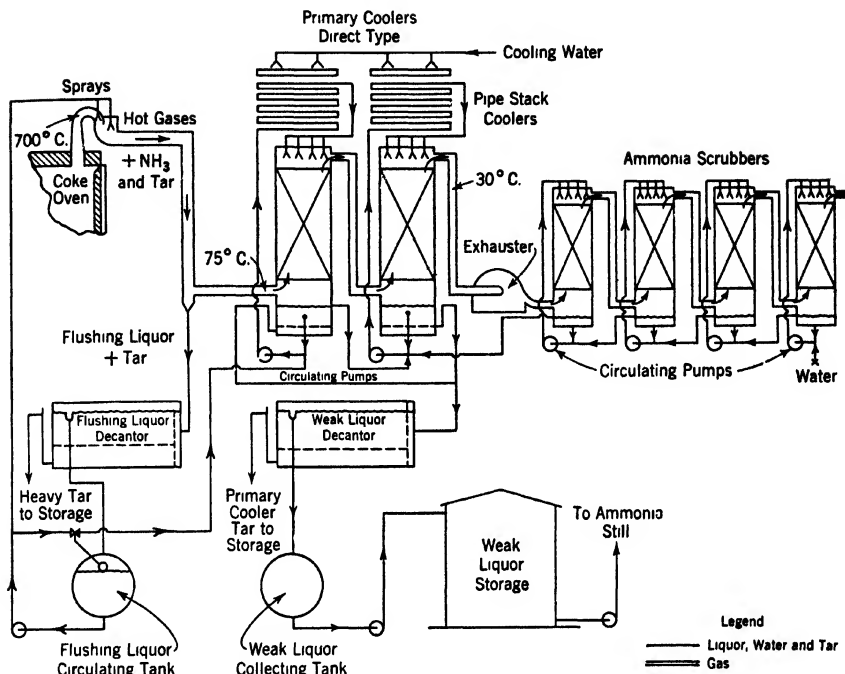
FIG. 2. Flow diagram for production of weak ammonia liquor by the indirect process.

passed. A direct primary cooler is a countercurrent scrubbing tower, filled with wooden hurdles or other packing. Hot aqueous condensate, which collects in the base of the tower, is recirculated continuously through water-cooled coils back into the top of the tower. Cooling of the gas is effected by direct heat exchange between gas and liquor.

Ammonia in the gas dissolves in the cool, primary cooler condensate, mainly as ammonium carbonate, sulfide, and cyanide. A light tar is also condensed, and tarry particles still entrained in the gas are precipitated. The aqueous condensate is decanted from the tar and added to the recirculated flushing liquor. The addition is more than sufficient to replace loss of water by evaporation in the mains before the primary cooler. The surplus flushing liquor thus produced is withdrawn from the circulation system continuously and collected in storage tanks. Figure 3 shows the primary coolers, tanks, and decanters in a typical byproduct coke plant. The cool gas from the primary cooler is pumped by the exhausters through the other byproduct-recovery and gas-purification operations.

INDIRECT PROCESS IN BYPRODUCT COKE PLANTS

In coke plants using the indirect process, the method of cooling the gas is the same as in the semi-direct process. From the primary coolers the gas is pumped to the ammonia scrubbers, wherein it is washed

Fig. 3. A direct-type primary cooler, tanks, and decanters in a byproduct coke plant   (Courtesy of the Koppers Company)

with water to recover the uncondensed ammonia.[4] A number of types of scrubbers are in use, all designed to remove the ammonia from the gas with the production of as concentrated a liquor as possible.[5] An efficient type, which has been commonly employed in American practice, consists of a series of chambers packed with wooden

4 Torrey, B., Jr, U. S Pat. 1.487.768 (1924).
5 Johns, W. H., J. Gas Lighting, 112, 189 (1911).   Barenfänger, J. Gasbeleucht., 63, 693 (1920).   Welttenhiller, H., Gluckauf, 68, 313–9 (1932).

hurdles, through each of which an ample stream of liquor is recirculated. The gas enters at one end of the set of chambers and passes through all in series. The scrubbing water is admitted to the last gas compartment and moves forward in countercurrent flow to the gas with constant recirculation in each compartment.

The ammonia scrubber has two functions: the ammonia in the gas must be reduced to the required limit, and a liquor with the maximum concentration of ammonia

must be produced. Since ammonia scrubbing is a typical gas-absorption process, the efficiency of recovery of the ammonia from the gas and the strength of the liquor will depend on such factors as partial pressures and vapor pressures of ammonia in gas and solution, respectively, temperature, volumes of gas and solution, contact area, and scrubber design.[6]

The ammonia is present in the scrubber liquor, not as ammonium hydroxide, but in the form of ammonium salts, principally sulfides, carbonates, and cyanide. Curves showing typical equilibriums between ammonia in gas and scrubber liquors are shown in Fig. 4.[7] Partial and total pressures of aqueous solutions of ammonia for use in ammonia-scrubber calculations have been determined by Terres and Weiser and by Hollings.[8] The influence of carbon dioxide and of ammonium chloride and phenol in solution on the vapor pressure of the ammonia at various temperatures has been studied by Pexton and co-workers,[9] and the results tabulated.

The following standards have been recommended by Bunte and Brückner[10] for ammonia scrubbers: hurdle-packed scrubbers, 25-30 square feet of scrubbing surface or 0.5 cubic foot of scrubber space packed with hurdles per 1,000 cubic feet of gas per 24 hours; and rotary scrubbers, 11 to 16 square feet of wetted surface per 1,000 cubic feet of gas per 24 hours.

OTHER CARBONIZING OPERATIONS

The production of ammoniacal liquors in other systems of coal carbonizing is in general similar to the practice in coke
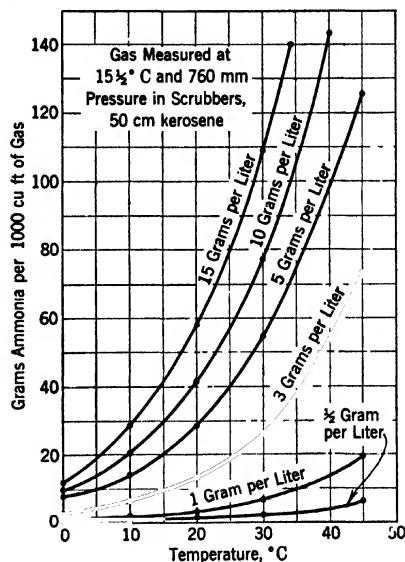
FIG. 4. The influence of temperature on the equilibrium between ammonia in coke-oven gas and ammonia liquors of different strengths.[7] (Courtesy McGraw-Hill Book Company.)

plants. By cooling the hot gases from the retorts, aqueous condensates are produced, which are handled in essentially the same manner.

VOLUME OF LIQUOR

The volume of · ammoniacal liquor produced by the carbonization of coal varies considerably, depending principally on the following factors:[11] (1) the amount of

6 Kowalke, O. L., Hougen, O. A., and Watson, K. M., *Chem. & Met. Eng.*, **32**, 506–10 (1925). Sherwood, T. K., and Kilgore, A. J., *Ind. Eng. Chem.*, **18**, 744–6 (1926).

7 Pacific Coast Gas Assoc., *Gas Engineers' Handbook*, McGraw-Hill Book Co., New York, 1934, p. 443.

8 Terres, E., and Weiser, H., *J. Gasbeleucht.*, **63**, 705–12 (1920); *Chem. Abs.*, **15**, 589 (1921). Hollings, H., *Gas J.*, **182**, 924–35 (1928); *Gas World*, **88**, 668–79 (1929); *Am. Gas J.*, **129**, No. 3, 59-60 (1929).

9 Pexton, S., Badger, E. H. M., and Silver, L., *J. Soc. Chem. Ind.*, **5**, 106-13T (1938).

10 Bunte, K., and Brückner, H., *Gas- u. Wasserfach*, **81**, 43 (1938).

11 Key, A., *Gas Works Effluents and Ammonia*, The Institution of Gas Engineers, London, 1938. p. 12.

moisture in the coal charged; (2) the water produced by decomposition of the coal, i.e., the water of constitution; and (3) the system of byproduct recovery. In vertical retorts, steam is often passed through the charge during carbonization. In such plants, the amount of steam so added and the efficiency of its decomposition in the retorts represent additional factors.

It is possible to give figures which indicate only approximately the volumes of liquors produced by the different systems of carbonization. The volumes produced per ton of normal bituminous coal as charged to different types of carbonizing plants are as follows:

Coke-plant, semi-direct
   process for ammo-
     nia recovery   15–25 gallons [12]
     indirect process   35–90 gallons [12]
     direct process   7–10 gallons [12]
Horizontal retorts   35–40 U. S. gallons [13]
Continuous, vertical re-
   torts   55–60 U. S. gallons [13]
Low-temperature   car-
   bonization   25 U. S. gallons [14]

Each percent of moisture in the coal is equivalent to 2.4 gallons of liquor per ton. Coal as charged frequently contains 4 to 5 percent moisture, which represents, therefore, 10–12 gallons of liquor per ton.

According to Morgan and Pettet,[15] the water of decomposition produced in the carbonization of dry coal may amount to 9.5 U. S. gallons per ton. They stated that the carbonization of moist coal in ordinary retorts may yield 25 gallons of liquor per

12 Page 649 of ref. 2. Marquard, F. F., *Am. J. Pub. Health,* **18,** 1497–500 (1928).

13 Page 13 of ref. 11. Parker, A., *Gas J.,* **179,** 101–3 (1927).

14 Lander, C. H., and McKay, R. F., *Low Temperature Carbonization,* Ernest Benn, London, 1924, pp. 193–4.

15 Morgan, G. T., and Pettet, A. E. J., *J. Soc. Chem. Ind.,* **56,** 109–14T (1937).

ton. The steam to vertical retorts may increase the liquor yield to 70 gallons per ton.

A balance showing the sources of the liquor under the conditions in a gas plant has been made by Tutweiler,[16] Table I. All

TABLE I

WATER BALANCE FOR LIQUOR FORMATION IN GAS PLANT [16]

	Percent of Coal	Gallons
Water in coal	2	4.8
Water of constitution	5.5	13.2
Fresh water added	9.6	23.1
Total water	17.1	41.1
Less water carried away in gas	0.46	1.2
Liquor produced	16.64	39.9

the ammonia, 4.5 to 5.5 pounds per ton of coal, was recovered as a liquor containing 1.5 percent ammonia.

The temperature of carbonization influences the volume of liquor and yields of byproducts. Data on liquor and ammonia yields obtained by Fieldner and his co-

TABLE II

AMMONIA AND LIQUOR PRODUCED AT DIFFERENT CARBONIZING TEMPERATURES [17]

Temperature		Yields in Percent, As Carbonized Basis	
°C	°F	NH₃	Liquor
500	932	0.007	5.6
600	1,112	.028	5.8
700	1,292	.095	5.9
800	1,472	.131	6.3
900	1,652	.117	5.1
1,000	1,832	.106	4.4

16 Tutweller, C. C., *J. Franklin Inst.,* **178,** 383–415 (1914).

17 Fieldner, A. C., Davis, J. D., Thiessen, R., Kester, E. B., Selvig, W. A., Reynolds, D. A., Jung, F. W., and Sprunk, G. C., *U. S. Bur. Mines, Tech. Paper* **525** (1932), 60 pp.

workers in the experimental coking of Pittsburgh Seam coal are shown in Table II.[17]

COMPOSITION OF LIQUORS

Ammoniacal liquors are usually clear solutions of a light shade of either brown, amber, or yellow. On exposure of the alkaline solution to the air, some of the compounds are oxidized, the color darkens, and the liquor becomes cloudy from the formation of insoluble products.

The composition of ammoniacal liquors depends chiefly on the following factors: (1) the system of carbonization employed; (2) the nature and moisture content of the coal; (3) the type of condensing and scrubbing system, and its method of operation.

The ammonia is present in the form of its salts, which may be classified as follows: [18]

1. "Free" salts, from which the ammonia is liberated by boiling. The ammonium salts include the carbonate, $(NH_4)_2CO_3$; bicarbonate, NH_4HCO_3; carbamate, $NH_4OCO(NH_2)$; sulfide, $(NH_4)_2S$; hydrosulfide, NH_4HS; polysulfide, $(NH_4)_2S_x$; and cyanide, NH_4CN.

2. "Fixed" salts, from which the ammonia can be liberated by boiling after the addition of an alkali. They may consist of the chloride, NH_4Cl; thiocyanate, NH_4SCN; ferrocyanide, $(NH_4)_4Fe(CN)_6$; sulfate, $(NH_4)_2SO_4$; sulfite, $(NH_4)_2SO_3$; thiosulfate, $(NH_4)_2S_2O_3$; and acetate, $NH_4C_2H_3O_2$.

The liquor also contains many organic compounds present in coal tar. The most important are the phenols, including both monohydric and polyhydric types. Smaller quantities of pyridine bases, neutral oils, and organic acids are present, together with other complex compounds about which little is known.

ANALYSES

Analyses of liquors from several American coke plants will serve to indicate the concentrations in which the compounds are found and the extent of the variations. These analyses must not be considered typical of any particular type of plant or method of byproduct recovery because the concentration of each compound is affected materially by many factors. (Table III.)

In Table IV are tabulated analyses of the liquors which were produced in an English coke plant carbonizing Welsh coal in Otto Hilgenstock ovens.[19] The analyses illustrate possible differences in the liquor from the different stages of the byproduct apparatus.

Table V contains analyses of liquor from horizontal and from vertical retorts, and Table VI the analyses from different parts of the byproduct apparatus belonging to an intermittent vertical retort plant.[20] Badger [21] and Pickles [22] have reported analyses of horizontal and vertical retort liquors.

No correlation between the nature of the coal and the composition of the liquor has been made. The coals commonly used for the production of coke and gas do not vary greatly in their nitrogen content, but a

[18] Morgan, J. J., *Manufactured Gas,* J. J. Morgan, New York, 1926, Vol. I, pp. 419–28.

[19] Bailey, T. L., *Ann. Rept. Alkali, &c., Works,* **63**, 22–3 (1927).

[20] See pp. 7–9 of ref. 11. See also Lunge, G., *Coal Tar & Ammonia: Pt. III, Ammonia,* D. Van Nostrand Co., New York, 1916, pp. 1258–66. Parrish, P., *The Design and Working of Ammonia Stills,* Ernest Benn, London, 1924, Chap. 8. *Trans. Inst. Gas Engrs.,* 1927 to date; *Gas J.* and *Gas World,* 1927 to date. Bailey, T. L., *Ann Rept. Alkali, &c., Works,* **64**, 31–5 (1928). See also p. 596 of ref. 2 and p. 445 of ref. 7.

[21] Badger, E. H. M., *J. Soc. Chem. Ind.,* **57**, 113T (1938).

[22] Pickles, L. S., *Gas World,* **91**, 340–5 (1929).

TABLE III

ANALYSES OF AMMONIACAL LIQUORS FROM COKE PLANTS

Process	Semi-Direct Sulfate		Total Recovery of Ammonia as Liquor	
Plant	A [23]	B [23]	C [24]	D [24]
Composition, grams per liter				
Ammonia, total	7.60	6.20	4.65	3.59
free	4.20	4.76	3.37	2.70
fixed	3.40	1.44	1.28	0.89
Carbon dioxide as CO_2	2.35	3.94	2.78	1.74
Hydrogen sulfide as H_2S	0.86	0.34	1.26	1.13
Thiosulfate as $H_2S_2O_3$	0.022	0.51		
Sulfite as H_2SO_3	2.84	....		
Sulfate as H_2SO_4	....	0.15		
Chloride as HCl	6.75	1.85		
Cyanide as HCN	0.062	0.05		
Thiocyanate as HCNS	0.36	0.42		
Ferrocyanide as $(NH_4)_4Fe(CN)_6$	0.014	0.039		
Total sulfur	1.014	0.57		
Phenols as C_6H_5OH	0.66	3.07		
Pyridine bases as C_5H_5N	0.48	0.16	1.27	0.98
Organic number (cc. $N/50$ $KMnO_4$ per l.)			4,856	3,368

[23] Koppers Company, private communication, 1933.
[24] Private communications, 1918–9.

TABLE IV

ANALYSES OF AMMONIACAL LIQUORS FROM DIFFERENT STAGES OF BYPRODUCT APPARATUS IN A COKE-OVEN PLANT [19]

	2 Annular Atmospheric Condensers	4 Water-Tube Condensers	3 Water Scrubbers	Collecting Well
Volume of liquor produced per ton of dry coal, gallons	4.5	23.5	33.0	.....
Temperature of gas entering, °C	68	61	24	.....
Character of liquor	Clear, colorless	Clear, colorless	Clear, colorless	Clear, faint straw
Analysis, grams per liter				
Ammonia, total	4.7	20.3	6.1	6.0
free	4.3	19.5	5.8	5.5
fixed	0.4	0.8	0.3	0.5
Sulfide as H_2S	0.95	3.08	2.35	1.02
Thiosulfate as $H_2S_2O_3$	0.11	0.21	0.14	0.29
Cyanide as HCN	0.07	0.10	0.13	0.05
Thiocyanate as HCNS	0.03	0.10	0.17	0.08
Phenol as C_6H_5OH	3.10	2.37	0.48	1.73
Color-producing bodies, including higher tar acids as $C_6H_4(OH)_2$	Trace	0	0	0
Oxygen absorbed, parts per million	6,150	4,850	1,080	4,200

TABLE V

COMPOSITION OF AMMONIACAL LIQUORS FROM
GAS RETORTS

Carbonizing System	Horizontal Retorts	Continuous Vertical Retorts
Composition, grams per liter		
Ammonia, free	15.0	10.0
fixed	5.0	3.3
total	20.0	13.3
Sulfide as H_2S	2.5	1.5
Cyanide as HCN	0.10	0.05
Thiosulfate as $H_2S_2O_3$	1.8	1.8
Thiocyanate as HCNS	2.0	2.0
Phenols as C_6H_5OH	2.5	3.5

TABLE VI

ANALYSIS OF AMMONIACAL LIQUORS FROM DIF-
FERENT STAGES OF BYPRODUCT APPARATUS,
INTERMITTENT VERTICAL OVEN PLANT

Description of Liquor	Retort House Liquor	Con- denser Liquor	Scrubber Liquor
Composition, grams per liter			
Ammonia, free	4.1	21.0	38.1
fixed	16.2	1.3	0.8
total	20.3	22.3	38.9
Sulfide as H_2S	0.2	5.0	8.4
Thiosulfate as $H_2S_2O_3$	3.4	0.5	0.5
Thiocyanate as HCNS	3.2	0.7	0.6
Chloride as HCl	22.9	1.8	2.6
Carbonate as CO_2	0.0	19.2	36.1
Phenol as C_6H_5OH	3.5	4.7	0.5
Oxygen absorption (4 hr at 27° C)			
Total, ppm	16,500	19,080	15,730
Total, omitting sul- fide, ppm	16,260	12,410	4,430
Specific gravity	1.022	1.02	1.04

variation in the chlorine content of the coal
should affect the proportion of fixed am-
monia.[25] This can be illustrated by com-
paring the chloride content in the liquor
produced during the coking of a coal from
Saxony which is notoriously high in chloride
with those from other German coals con-
taining a normal chloride content, Table
VII.

In direct-process plants the gas leaves
the saturators at above 70° C, saturated
with water vapor. Parker [26] has reported
the analysis of an aqueous condensate which
separated in the gas condensers of one
such plant: total ammonia, 0.51; cyanide
as HCN, 0.06; sulfide as H_2S, 0.04; thio-
sulfate as $H_2S_2O_3$, 0.36; thiocyanate as
HCNS, 0.24; phenols as C_6H_5OH, 6.30
grams per liter respectively; and oxygen
absorbed, 12,460 parts per million. A small
amount of liquor, that had been condensed
in the tar extractor which precedes the
saturator in a direct-process plant, con-
tained almost exclusively fixed ammonium
salts.[26, 27]

OTHER INORGANIC COMPOUNDS

In addition to ammonium salts the liquors
contain small amounts of other inorganic
compounds, such as iron salts which may
come from plant equipment, and sodium
or calcium salts from scrubber water. De-
mann and Ter-Nedden,[28] in their phos-
phorus balance for the coke-oven operation,
found that 2 percent of the phosphorus in
the coal charged appeared in the liquor
and tar.

ORGANIC MATTER

High-temperature liquors usually contain
between 2 and 5 grams per liter of mono-
hydric phenols, which include phenol, cre-
sols, xylenols, and higher acids, all deter-
mined together as C_6H_5OH. The total
phenolic content of a high-temperature
liquor was found by Morgan and cowork-
ers [29] to be much less than that in the cor-
responding amount of low-temperature liq-

25 See p. 11 of ref. 11.

26 Parker, A., Gas J., 179, 172–5 (1927).
27 See pp. 589 and 627–30 of ref. 2.
28 Demann, W., and Ter-Nedden, W., Tech.
Mitt. Krupp, 4, 1–6 (1936).
29 Morgan, G. T., and Pettet, A. E. J., J. Soc.
Chem. Ind., 50, 72-4T (1931).

TABLE VII

Ammonium Salts in Liquors from German Coals [30]

Gas liquor from	Chemnitz	Another City in Saxony	Bonn	Trier	Zurich
Source of coal	Zwickauer	Zwickauer	Ruhr	Saar	Saar
Composition, grams per liter:					
Total ammonia	12.09	9.40	18.12	15.23	3.47
Ammonium thiosulfate	1.036	1.628	5.032	2.072	0.296
Ammonium sulfide	0.340	0.646	6.222	3.468	1.428
Ammonium bicarbonate	1.050	1.470	2.450 ⎱	33.763	5.856
Ammonium carbonate	4.560	7.680	33.120 ⎰		
Ammonium sulfate	0.462	0.858	1.320 ⎱	4.922	1.926
Ammonium chloride	30.495	17.120	3.745 ⎰		
Total ammonium salts	37.943	29.402	51.889	43.225	9.506

[30] Lunge, G., and Köhler, H., *Die Industrie des Steinkohlenteers und des Ammoniaks*, F. Vieweg & Sohn, Braunschweig, 1912, Vol. 2, p. 183.

TABLE VIII

Analyses of Coal and the Liquors Produced Therefrom by Carbonization at High and Low Temperatures [29]

	Semi-Continuous		Vertical		Horizontal
Carbonization temperature, °C	625	625	625	625	1,350
Coal	Shafton	Dalton Main	South Hetton	Mitchell	Main
Approximate analysis, %					
Moisture	6.0	2.7	2.0	1.4	
Volatile	39.1	34.5	34.1	31.8	
Fixed carbon	50.0	59.4	59.4	60.3	
Ash	4.9	3.4	4.5	6.5	
Ultimate analysis, %					
Ash	5.1	3.49	4.56	6.59	
Carbon	75.5	81.11	81.31	80.66	
Hydrogen	5.0	4.95	5.33	5.05	
Nitrogen	2.0	1.67	1.73	1.59	
Sulfur	2.1	0.96	1.67	1.62	
Oxygen	10.3	7.82	5.40	4.49	
Steam to retorts, % coal charged	11.0	9.7	11.2	10.0	....
Moisture in coal as charged, %	9.0	2.2	3.1	4.0	1.6
Yield of liquor, gal/ton	42.6	33.2	24.0	26.6	18.0
Analysis of liquor, grams/liter					
Neutral oil	0.8	0.5	0.7	0.6	0.4
Bases	Trace	Trace	Trace	Trace	Trace
Carboxylic acids	1.7	1.2	1.4	2.1	0.6
Phenols					
Total	12.5	9.8	7.4	5.8	4.0
Phenol	1.3	0.97	0.41	0.74	1.44
Catechol	0.98	Trace	Trace	0.01	Nil
Total ammonia	7.4	8.0	9.0	8.4	30.7
Total sulfur	3.5	2.0	5.3	4.4	5.3
Weight of phenol in liquor, lb/ton	6.17	3.44	1.92	1.72	0.72

uor from the same coal, but the high-temperature liquor was characterized by a higher content of phenol itself. Some comparative data are shown in Table VIII.

Polyhydric phenols have been found, particularly in liquors from vertical retorts. Bailey [31] has published the results of determinations on the polyhydric phenols which absorb oxygen in the liquors from three horizontal and three vertical retort plants, respectively. The concentrations are expressed as catechol in Table IX. Currey [32]

TABLE IX

POLYHYDRIC PHENOLS IN RETORT LIQUORS [31]

		Parts per Million
Horizontal retorts, Works	A	190
	B	160
	C	270
Vertical retorts, Works	D	600
	E	1,150
	F	2,240

found that polyhydric phenols, present in a vertical-retort liquor to the extent of 0.05 to 0.1 percent by volume, were responsible for a red color in the water of the Parramatta River. They consisted principally of catechol, but resorcinol and small quantities of trihydric phenols were also present. In addition a methyl ether (possibly guaiacol) was detected.

Liquors from high-temperature coking operations contain pyridine bases. The concentrations in the liquors of Table III ranged from 0.16 to 1.68 grams per liter.

Ammoniacal liquors also probably contain organic sulfur compounds. Sulfur balances were made by Bailey [33] for the compounds in an ammoniacal liquor and a still waste with the results shown in Table X.

TABLE X

SULFUR BALANCE IN AMMONIACAL LIQUOR [33]

Liquor	Ammoniacal grams per liter	Waste from Still grams per liter
Sulfur, present as sulfate	0.18	0.20
Sulfur, present as sulfide	0.99	....
Sulfur, present as thiocyanate	1.38	1.49
Sulfur, present as thiosulfate	1.24	0.80
Total sulfur in compounds	3.79	2.49
Total sulfur found	3.90	2.52
Difference	0.11	0.03

The difference in the total sulfur contents was not significant in the still waste, but Bailey considered it possible that organic sulfur compounds, other than those indicated, were present in the ammoniacal liquor.

COMPOSITION OF LOW-TEMPERATURE LIQUORS

The liquors produced by the carbonization of coal at temperatures below 700° C differ greatly from those produced at higher temperatures. According to Fischer and Lessing [34] the aqueous liquors from the low-temperature carbonization of both bituminous and brown coal have an acid reaction. Only minute amounts of nitrogen enter the liquor; the major portion remains in the semicoke. Acetone and catechol were found in liquors from low-temperature carbonization of both brown and bituminous coals. Methyl alcohol was also present in the liquor from the brown coal.

Jones and Wheeler [35] reported that bituminous coals when distilled in a vacuum of

[31] Bailey, T. L., *Ann. Rept. Alkali, &c., Works,* **63,** 26 (1927).

[32] Currey, G. S., *J. Soc. Chem. Ind.,* **42,** 379-86T (1923).

[33] Bailey, T. L., *Ann. Rept. Alkali, &c., Works,* **65,** 26 (1929).

[34] Fischer, F., and Lessing, R., *Conversion of Coal into Oils,* Ernest Benn, London, 1925, p. 43.

[35] Jones, D. T., and Wheeler, R. V., *J. Chem. Soc.,* **105,** 140-51 (1914).

5 to 40 millimeters at temperatures up to 430° C gave an aqueous liquor containing hydrochloric acid and traces of ammonium chloride. Pictet and Bouvier [36] reported the formation of an acid liquor by the distillation of coal at 15 to 17 millimeters pressure at 450° C. No ammonium salts were found.

Sinnatt, King, and Linnell [37] examined the aqueous distillates from a medium caking coal distilled in horizontal retorts at temperatures ranging from 400 to 700° C. The concentration of the ammonia in the liquor increased over 1,000 percent as the temperature of coking was increased from 400 to 700° C (Table XI).

carbonization of a noncoking, ortho-lignitous coal at 625° C in vertical retorts amounted to 71.4 U. S. gallons per ton of the coal. Of this, 20.2 gallons represented water of decomposition of the coal, and 25.7 gallons was introduced as steam to the retorts. The total ammonia in the liquor amounted to 5.5 grams per liter, and the total sulfur, 2.1 grams per liter. Groups of organic compounds were present in the following concentrations: neutral oils 0.2, bases <0.1, phenols 9.2, and carboxylic acids 3.7 grams per liter, respectively.

A considerable proportion of the compounds in each group consisted of resins. The analysis of the neutral oils is shown in

TABLE XI

Temperature of carbonization, °C	400	450	500	550	600	650	700
Yield of aqueous distillate, percent by weight of coal	5.6	7.01	7.92	7.70	8.12	8.20	7.18
Reaction of liquor	Acid	Acid	Acid	Neutral	Alkaline	Alkaline	Alkaline
Color	Pale yellow	Pale yellow	Purple	Yellow	Red	Nil	Red
Specific gravity at 15° C	1.003	1.011	1.006	1.009	1.009	1.015	1.016
Ammonia, grams per liter	1.24	2.27	3.23	6.61	12.06	11.64	15.68
Chlorine " " "	2.61	6.80	9.72	12.86	18.41	14.35	15.24
Iron " " "	0.44	0.55	0.37	0.24	0.28	0.21	0.15

Liquors from two low-temperature operations were analyzed by Bailey,[38] Table XII.

Probably the most detailed studies of the organic constituents of ammoniacal liquors have been made by Morgan and his coworkers.[15, 39] The aqueous liquor from the

36 Pictet, A., and Bouvier, M., Ber., 46, 3342–53 (1913).
37 Sinnatt, F. S., King, J. G., and Linnell, W. H., J. Soc. Chem. Ind., 45, 385-93T (1926).
38 Bailey, T. L., Ann. Rept. Alkali, &c., Works, 64, 35 (1928).
39 Morgan, G. T., Pratt, D. D., and Pettet, A. E. J., J. Soc. Chem. Ind., 48, 89-93T (1929). Morgan, G. T., and Pettet, A. E. J., ibid., 50, 72-4T (1931).

Table XIII. Among the bases, aniline, pyridine, and α-picoline were identified. Resin amines were also present.

In a mixture of fatty acids, which included formic, acetic, propionic, n-butyric, and n-valeric, acetic acid predominated. Oxalic acid and a mixture of complex acids, termed resinoic acids, were found. From 120 gallons of liquor phenols, polyhydroxy phenols, and resinolic acids (compounds less acidic than the resinoic acids yet more acidic than resinols) were recovered in amounts equivalent to the following concentrations: phenol 1.53, catechol 0.94, and

TABLE XII

ANALYSES OF AMMONIACAL LIQUORS FROM LOW-TEMPERATURE CARBONIZATION OF COAL [18]

Retorts internally heated, with addition of steam

Process	A	B
Character of liquor	Yellow-brown, cloudy	Yellow, clear
Ammonia, free	7.2 grams per liter	2.4 grams per liter
fixed	0.9	0.6
total	8.1	3.0
Sulfide as H_2S	0.3	0.3
Cyanide as HCN	Nil	Nil
Monohydric phenols as C_6H_5OH	4.24	2.44
Thiocyanate as HCNS	0.16	0.07
Thiosulfate as $H_2S_2O_3$	0.23	0.39
Color-producing bodies (including higher tar acids) as $C_6H_4(OH)_2$	10.0	0.6
Oxygen absorbed (permanganate 4-hr test at 27° C)	13,020 ppm	5,650 ppm

TABLE XIII

NEUTRAL OILS FROM AMMONIACAL LIQUOR [34]

	Percent
Resins	7.5
Compounds precipitated by $FeCl_3$ and HCl	12.0
Oxygenated compounds extracted by $FeCl_3$ and HCl	9.5
Unsaturated hydrocarbons	42.5
Aromatic hydrocarbons	
(a) Forming crystalline picrates	3.5
(b) Not forming crystalline picrates	8.0
Saturated hydrocarbons	12.0
Loss	5.0

resinolic acids 1.035 grams per liter, respectively. Also o- and m-cresols, isohomocatechol, homocatechol, resorcinol, and quinol were identified in various fractions of the phenolic matter. Analyses of the liquors from a number of coals indicated that the phenolic content depended largely upon the oxygen content of the coal (cf. Table VIII). The following concentrations of sulfur-containing compounds were also found, all expressed as weight of sulfur: sulfide sulfur 1.02, sulfite sulfur 0.24, thiosulfate sulfur 0.65, sulfate sulfur 0.44, and

thiocyanate sulfur 0.2 gram per liter, respectively.

An aqueous liquor from low-temperature carbonization, which was studied by Brittain, Rowe, and Sinnatt,[40] had a straw-yellow color and was faintly acid in reaction. On neutralization, a gray precipitate separated which contained 24.4 percent iron. In Table XIV are listed the compounds which were detected; in some cases the concentration was determined. About 15 percent of the total organic matter consisted

TABLE XIV

ORGANIC COMPOUNDS IN LOW-TEMPERATURE LIQUOR [40]

Ammonia	2.9 grams per liter
Pyridine bases	0.4 gram per liter
Secondary bases	Present
Di- and triethylamine	Present
Phenols as C_6H_5OH *	0.6 gram per liter
Catechol	Present
Formic and acetic acids	Present
Acetaldehyde	Present
Acetone	Nil

* Also present: 43 percent o-cresol, m- and p-cresol, and xylenols.

40 Brittain, A., Rowe, F. M., and Sinnatt, F. S., *Fuel*, 4, 337–40 (1925).

of resinous compounds. A dilute, aqueous solution of the resinous matter had a brown color when alkaline, but the color was discharged when acid.

The low-temperature carbonization of Lohberg gas coal gave 7 to 8 percent of a gas liquor containing 0.1 percent by weight of phenolic substances. No measurable quantity of phenol itself was detected in the products by Gluud.[41] The amount of catechol in the liquors amounted to 0.0056 percent by weight of the coal.

Széki and Romwalter[42] reported that a liquor from low-temperature carbonization contained the compound $2NH_4HCO_3 \cdot (NH_4)_2CO_3$. The phenols absorbed both oxygen and sulfur and appeared to be suitable for ink production.

Börnstein[43] isolated catechol from the ether extract of another liquor.

The organic matter in a liquor from the low-temperature carbonization of Utah coal was present in the following proportions, according to Brown and Branting:[44] carboxylic acids 0.39, phenols 2.25, bases 0.082, and neutral oils 0.1 gram per liter, respectively. The phenols included phenol, 33 percent; cresols (mainly m- and p-), 18 percent; catechol, 4 percent; higher phenols, 4 percent; and tar resins, 37 percent. Ammonia in the liquor amounted to 0.397 gram per liter. The liquor was neutral to litmus.

Methyl alcohol was identified in the aqueous liquor from the low-temperature carbonization of coals in rotating retorts by

Kester and Daeschner.[45] The presence of phenol, acetone, acetic acid, and methyl ethyl ketone was reported.

Oda[46] found methanol, together with acetic acid, and traces of phenol, in the aqueous condensate from the carbonization of lignite.

MacLaurin[47] reported that the aqueous liquor from MacLaurin producers contained resinous matter which dyed wool in gray or yellow shades. Neither ferrocyanide nor thiocyanate was detected in this liquor.

Rosenthal[48] concentrated a large volume of retort liquor produced in the distillation of brown coal and analyzed much of the organic matter. The mixture of organic acids included many sulfur-containing and unsaturated compounds. Acetic, propionic, n-butyric, and valeric acids were identified by formation of their ethyl esters, and saturated acids boiling to 300° C were separated. In the liquor were also found catechol; phenols boiling from 200 to 300° C; pyridine; methyl indole; unsaturated and saturated aldehydes, including acetaldehyde; ketones, of which acetone and methyl ethyl ketone were identified; methyl alcohol; and acetonitrile. The presence of benzaldehyde was indicated.

Waste waters from a plant for the carbonization of peat were found by Nevyazhskaya and her coworkers[49] to contain 45–47 grams per liter of acetic acid, 12–20 grams per liter nitrogen compounds, and 5–18

41 Gluud, W., *Ges. Abhandl. Kenntnis Kohle*, 3, 66–74 (1918).

42 Széki, J., and Romwalter, A., *Roy. Hung. Palatin-Joseph Univ. Tech. Econ. Sci., Pub. Dept. Mining Met.*, 8, 116–26 (1936) ; *Chem. Abs.*, 32, 3124 (1938).

43 Börnstein, E., *Ber.*, 35, 4324–5 (1902).

44 Brown, R. L., and Branting, B. F., *Ind. Eng. Chem.*, 20, 392–6 (1928).

45 Kester, E. B., and Daeschner, H. W., *U. S. Bur. Mines, Carnegie Inst. Tech. & Mining Met. Advisory Boards, Coop. Bull.* 54 (1932), 31 pp.

46 Oda, R., *J. Soc. Chem. Ind. (Japan)*, 33 (Suppl. Binding), 441-4 (1930) ; *Chem. Abs.*, 25, 795 (1931).

47 MacLaurin, R., *J. Soc. Chem. Ind.*, 36, 620–6 (1917).

48 Rosenthal, T., *Z. angew. Chem.*, 14, 665–7 (1901), 16, 221–5 (1903).

49 Nevyazhskaya, L. M., et al., *Khim. Tverdogo Topliva*, 8, 286–94 (1937) ; *Chem. Abs.*, 32, 1429 (1938).

grams per liter of compounds which could be brominated, calculated as phenol.

SUSPENDED MATTER IN AMMONIACAL LIQUORS

Ammoniacal liquors may contain suspended matter. Durand [50] found that the floating material in the residual water of coking plants consisted largely of carbon dust enveloped by tarry matter. The wastes heavier than·water consisted largely of silicon and calcium compounds, carbonates, sulfates, and sulfides.

PROPERTIES OF LIQUORS

CHANGES CAUSED BY OXIDATION

The oxidizing action of the air produces important changes in an ammoniacal liquor. The color darkens from amber to a muddy brown, and a brown precipitate settles. Bailey [51] showed that this darkening in color was a property characteristic of catechol, hydroquinone, and pyrogallol among other polyhydric phenols. In laboratory tests made by shaking dilute ammoniacal solutions of several phenols with air, the following color changes were observed: catechol turns brown, color develops rather slowly; resorcinol remains practically colorless; hydroquinone turns yellow, color changes rapidly to pink brown with an intensity about one-sixth that of catechol, weight for weight; and pyrogallol turns brown-yellow, color develops rapidly with intensity about 70 percent that of catechol, but the tints are difficult to match.

Air oxidation is responsible for the formation of polysulfides, thiocyanates, and thiosulfates. These compounds are not found in appreciable quantities in the gas from the ovens but are produced subse-

quently by oxidation of cyanide and sulfur.[52]

According to Morgan [53] the following reactions probably occur:

$$4(NH_4)_2S + O_2 + 2H_2O \rightarrow$$
$$2(NH_4)_2S_2 + 4NH_4OH$$
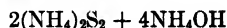
Sulfite is produced by oxidation of the sulfide:

$$2(NH_4)_2S + 3O_2 \rightarrow 2(NH_4)_2SO_3$$
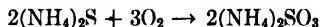
The sulfite and polysulfides in turn react to form thiosulfate:

$$(NH_4)_2S_2 + (NH_4)_2SO_3 \rightarrow$$
$$(NH_4)_2S_2O_3 + (NH_4)_2S$$
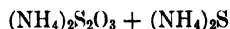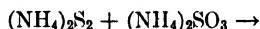
The final oxidation product is ammonium sulfate, but only a small proportion of the sulfur reaches this stage

Curphey and Bailey [54] ascribed the formation of the thiocyanate mainly to reaction of oxygen, ammonium sulfide, and cyanide in the cooler parts of the condensing system where conditions favor the formation of polysulfide:

$$(NH_4)_2S_2 + NH_4CN \rightarrow (NH_4)_2S + NH_4CNS$$
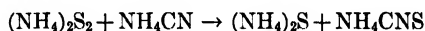
Curphey used the reaction as a means for the estimation of polysulfide in the liquor. The concentration of ammonium thiocyanate was determined before and after addition of cyanide. The increase was caused by reaction of the cyanide. The effect of these reactions on the composition of the liquor is shown in the analyses of a liquor from inclined vertical retorts reported by Bailey,[55] Table XV.

The importance of cyanide in the formation of the thiocyanate in liquor was also

[50] Durand, R., *Bull. sci. pharmacol.*, **34**, 15–20 (1927).

[51] Bailey, T. L., *Ann. Rept. Alkali, &c., Works*, **64**, 27 (1928).

[52] See p. 8 of ref. 11.

[53] See pp. 420–1 of ref. 18.

[54] Curphey, W. S., *Gas J.*, **143**, 69 (1918). Bailey, T. L., *Ann. Rept. Alkali, &c., Works*, **61**, 15–6 (1925).

[55] Bailey, T. L., *J. Soc. Chem. Ind.*, **44**, 835–45 (Chem. Ind. Rev.) (1925).

TABLE XV

ANALYSIS OF LIQUOR FROM INCLINED VERTICAL RETORTS [55]

Liquor	Fresh	After Storage for at Least Three Months
Total sulfur, grams per liter	8.55	9.12
$H_2S : NH_3$ ratio	0.311 : 1	0.306 : 1
Thiosulfate, percent of total sulfur	3.1	16.4
Sulfide, percent of total sulfur	72.8	21.2
Sulfate, percent of total sulfur	0.7	4.6
Thiocyanate, percent of total sulfur	23.4	57.9
HCN, grams per liter	0.68	Nil

shown by Bailey.[54] In two British plants, scrubbers for removal of the cyanides from the gas at an early stage of the gas-treatment process were installed. The effects of their operation on the thiocyanate content of the spent liquor are shown in Table

LOSS BY EVAPORATION

When ammoniacal liquors are exposed to the air, ammonia is lost by evaporation. According to Curphey,[57] this loss can largely be prevented by covering the liquor with a layer of mineral oil; 0.1 inch is satisfactory. The loss in ammonia in a period of 80 days varied from 20 to 40 percent, but where oil was used it was only 0.3 to 0.5 percent.

EFFECTS ON MATERIALS OF CONSTRUCTION

Ammoniacal liquors are commonly handled and stored in steel which lasts reasonably well in service. Corrosion tests on steel and other metals in ammoniacal liquors under plant conditions have been made by Fraser and Cox.[58] Their results showed

TABLE XVI

EFFECTS OF OPERATION OF CYANIDE SCRUBBERS ON CYANIDE CONTENT OF SPENT LIQUOR [54]

	Cyanide Recovery Plant	Air Admitted to Crude Gas	CNS in Spent Liquor grams per liter
Williams process	Working	None	0.5
British Cyanide Co.'s Process			
August, 1923	Not working	At inlet to exhausters	3.0
April, 1924	Working	At purifiers	1.65
October, 1924	Working badly	At purifiers	2.35
February, 1925	Working	At purifiers	1.65

XVI. Bailey stated that thiocyanate is also formed by reaction of carbon disulfide and ammonia or ammonium polysulfide.

Grossman [56] claimed that weak ammonia liquors on standing gain in concentration of ammonia owing to conversion of the cyanide to ammonium carbonate, and he found that ferrocyanides are formed by the reaction of ferrous sulfide and ammonium cyanide.

that the deposition of tar on the metal was effective in minimizing corrosion.

The presence of oxygen in storage tanks has been blamed by Ott [59] as a factor in corrosion, and he recommended that steel tanks be kept full of an inert gas in order

56 Grossman, J., J. Gas Lighting, 96, 526–8 (1907).

57 Curphey, W. S., Gas World, 63, 539 (1915) ; J. Gas Lighting, 132, 424 (1915) ; Chem. Trade J., 57, 596 (1915) ; J. Soc. Chem. Ind., 35, 1001- 2 (1916).

58 Fraser, O. B. J., and Cox, G. L., Proc. Am. Gas Assoc., 1939, 605–16.

59 Ott, E., Chem.-Ztg., 41, 161 (1917) ; J. Soc. Chem. Ind., 36, 539 (1917).

to prevent the destructive action. Ammonium cyanide has also been cited as a corrosion factor.[60]

Ott [59] reported that, in concrete tanks, ammonium salts in the liquor attacked the free lime to form soluble calcium salts. Concrete was only partly protected by coating the interior with tar. A deleterious action of liquor on concrete has also been observed by Donath and by Haas.[61] According to Haas, both ammonium carbonate and ammonium sulfide attacked the iron in the concrete. The carbonate dissolved part of the iron, and the sulfide converted iron compounds to ferrous sulfide. When the sulfide was subsequently oxidized, the coherence of the concrete was diminished. Disintegration was avoided by preventing access of air to the ferrous sulfide.

Idashkin,[62] on the other hand, found that concrete specimens after submergence for 28 days in ammoniacal liquor had increased in tensile and compressive strength. He recommended the replacement of steel tanks with concrete for storing ammoniacal liquor.

SPECIFIC HEAT

The specific heat of an ammoniacal liquor, determined by Schairer [63] in a calorimeter to which measured quantities of heat were supplied electrically, was 1.008.

DISTILLATION OF LIQUOR

In most coke and gas plants ammoniacal liquor is distilled and the ammonia is recovered as ammonium sulfate by either the semi-direct or the indirect processes, as crude or pure concentrated ammonia liquor, or as ammonium bicarbonate.

The ammoniacal liquor is distilled with direct steam in continuous, countercurrent stills. A typical still (see Fig. 5) consists of three main parts, for which a flow diagram is shown in Fig. 1: (1) the "free still" in which ammonia from the free ammonium salts is vaporized, together with hydrogen sulfide, carbon dioxide, hydrocyanic acid, some phenols, pyridine, and portions of the other organic compounds; (2) the lime reservoir, in which milk-of-lime is added to the hot liquor in order to decompose the fixed salts; and (3) the "fixed still" in which the ammonia, formerly fixed, is vaporized. An additional portion of the organic matter may be volatilized in this fixed still. In some plants where receipts from sale of the ammonia have not justified the cost of recovery, liming of the liquor is omitted, and an effluent containing fixed ammonia is discharged from the base of the free still. The lime reservoir and fixed leg, if present, are not used.

The steam for distillation is introduced directly at the base of the fixed still and leaves at the top to enter the base of the free still. The mixture of steam, ammonia, acidic gases, and other compounds from the top of the free still is usually cooled in a dephlegmator. The temperature of the vapors from the dephlegmator is determined largely by local conditions and the products to be manufactured.

Vapor-pressure data are seldom employed for the design of the stills, because of the wide variations in liquor composition which are encountered. The stills are usually designed on the basis of empirical observation and practical experience.[64]

60 Anon., *Gas World*, **58**, 667 (1913).

61 Donath, E., *Chem. Ind.* (*Ger.*) *Nachr.-Ausgabe*, **34**, 123–5 (1911). Haas, B., *Chem.-Ztg.*, **46**, 39 (1922).

62 Idashkin, S. I., *Coke & Chem.* (*U.S.S.R.*), Nos. 5 and 6, 19–23 (1933); *Chem. Abs.*, **29**, 3130 (1935).

63 Schairer, W., *Glückauf*, **72**, 454–6 (1936).

64 See pp. 601–2 of ref. 2.
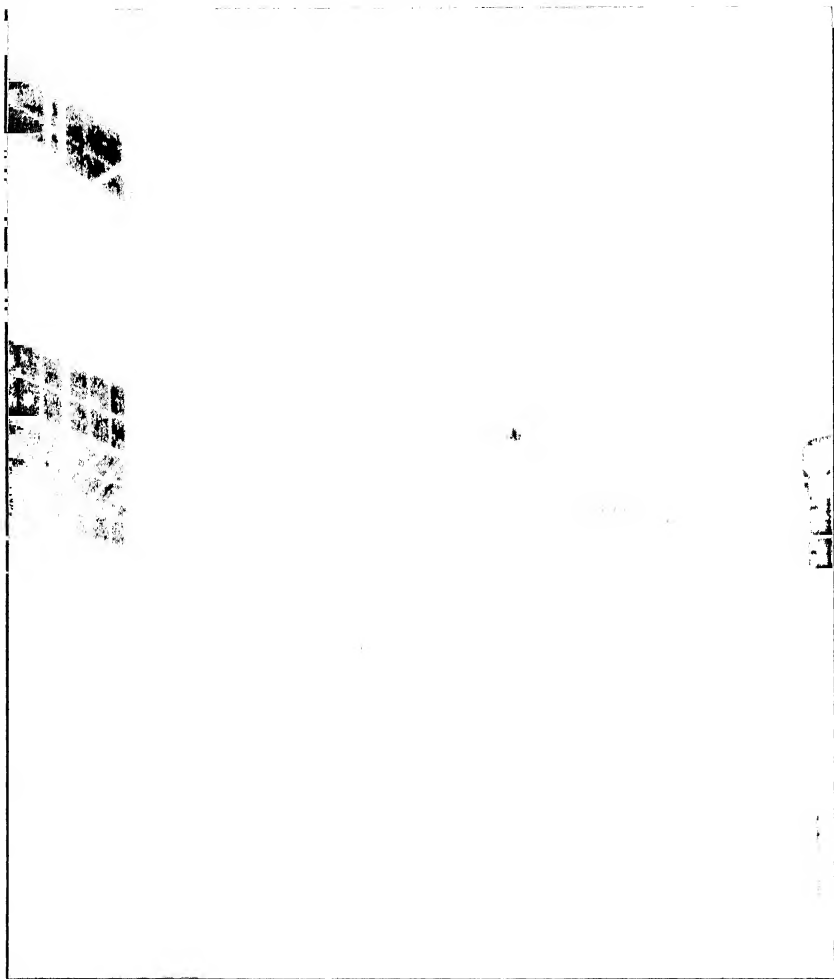
Fig. 5. Fixed and free ammonia stills and lime reservoir. (Courtesy of the Koppers Company.)

Piron [65] has described a method by which the vapor-pressure ratios between ammonia in steam and liquor may be determined for use in studies on still design and operation. Small portions are distilled from a sample of the liquor and condensed. The concentrations of ammonia in the liquor and the condensate are determined after each distillation and used in the preparation of vapor-pressure curves characteristic of still conditions.

[65] Piron, E., *Chem & Met. Eng*, **26**, 317–20 (1922).

The great majority of ammonia stills are of the bubble-plate type and are built of flanged cast-iron sections. A large number of plate arrangements have been proposed, and many of the types used in foreign practice have been illustrated by Parrish.[66] He recommended a shallow seal for the bubble caps on the plates, 1 inch rather than 4 inches. The best vapor velocity through a section, he concluded, was 5 to 10 feet per second. Older types of stills have been described by Lunge.[67] Both works include information on intermittent stills, a type which is practically obsolete. Stills without bubble plates but filled with Raschig or carbon rings have also been described.[68]

Easy access to each section of the still in order to permit cleaning is essential. This and the relatively heavy cast-iron construction have greatly influenced design. Each section is provided with a number of manholes large enough to permit removal of accumulations of tar from the free still and deposits of lime salts from the fixed still. Complete dismantling of the still may be necessary at times, for which provision must be made.

The most severe corrosion condition is encountered in the dephlegmator. These sections are usually made of cast iron with aluminum tubes, which have largely replaced cast-iron tubes. Some dephlegmator shells have been protected with concrete linings. Aluminum can be safely used for the manufacture, transport, or storage of the ammonia from coke ovens.[69]

The use of vacuum stills has been proposed, but consideration of the relative vapor pressures of ammonia and water at reduced pressure has led Parrish[66] to the conclusion that no great saving in steam consumption is likely to occur, whereas an additional expenditure of steam is necessary to operate the vacuum pump and the pump for withdrawing the effluent liquor from the still.

Preheating of the liquor feed to the still by utilizing the waste heat in the vapors or the effluent from the still is practiced. In general the low rate of heat transfer, the necessity for periodic cleaning of the preheater, and the additional complications have rendered such heat interchange unattractive in most American plants.

The milk-of-lime is made by slaking quicklime in a mixing tank and adding sufficient water so that a uniform suspension can be pumped to the still. Batch slakers and mixers are commonly employed, but continuous apparatus has also been used. Table of strengths for milk-of-lime are given by Gluud and Jacobson and in the *Gas Engineers' Handbook*.[70] One pound of lime per gallon of milk-of-lime is the concentration used in many plants.[71]

Although the milk-of-lime is screened, some of the finer solids from the lime are pumped to the still. The lime reservoir should therefore be of sufficient size to permit the settling out of these solids and prevent their accumulation on the still trays. On the other hand, it must not be so large that the lime will settle out in this vessel. The sediment in the bottom is flushed out periodically. A little steam is continuously admitted at the bottom in order to keep the lime in suspension.

The use of bases other than lime, such as caustic soda or soda ash, is ruled out

[66] Parrish, P., *The Design and Working of Ammonia Stills*, Ernest Benn, London, 1924, 283 pp.

[67] Lunge, G., *Coal Tar and Ammonia: Pt. III, Ammonia*, D. Van Nostrand Co., New York, 1916, pp. 1344–450.

[68] Tran, A., *Gas J.*, **226**, 472–4 (1939).

[69] Bally, J., *Rev. aluminium*, **15**, 1155–66 (1938).

[70] See p. 600 of ref. 2 and p. 446 of ref. 7.

[71] Private communication, 1928.

from the standpoint of cost. Direct addition of slaked lime to the liquor would reduce the volume of still waste, but this alkali is more expensive than ordinary lime, and mechanical difficulties are encountered in its uniform addition.[72] Limestone reacts slowly with ammonium chloride at the boiling point.[73] The use of alkaline earth or zinc carbonates at elevated pressures, 20 pounds per square inch, has been patented by Sperr.[74] Magnesia may also be used for decomposing ammonium chloride.[75] Lunge [76] indicated that the cost of the magnesia would necessitate its recovery.

For efficient operation of an ammonia still, uniform steam flow, feed, and other conditions are essential. Uniform operation becomes more imperative the more complicated the still, for instance in the stills for the production of *aqua ammonia*.

VOLUME AND CHARACTERISTICS OF STILL WASTE

The waste liquor from an ammonia still has a brown or red-brown color. When properly limed and distilled it has a characteristic sweetish, not unpleasant odor. Still waste from which the ammonia has been removed by addition of lime is alkaline, according to Key,[77] and oxidation of the higher tar acids takes place very rapidly, resulting in the production of a deep color almost as soon as the liquor leaves the still. Waste from which only the free ammonia has been removed is almost neutral in reaction, but oxidation proceeds fairly rapidly if the liquor is shaken in air.

The volume of waste depends on the amount of steam added for preheating, the amount of dephlegmation, the efficiency of the still, the strength of the liquor, and the volume of milk-of-lime added. To this must be added, in the indirect sulfate process, any condensed vapors from the saturators.

In semi-direct sulfate plants the total volume of the waste usually amounts to from 150 to 160 percent of the volume of the original liquor. The milk-of-lime usually represents 10 to 20 percent of the volume of the waste.[78] When the fixed ammonia is not recovered the volume of waste is smaller, usually from 125 to 135 percent of the volume of the original liquor. The volume of still waste from a direct-process plant is approximately one-third that which would be produced in a semi-direct plant.

According to Marquard,[79] with the semi-direct system of ammonia recovery, 20 gallons of still waste are produced per net ton of coal carbonized. Plants using washed coal containing about 8 percent free water and 5 percent water of constitution produce about 28 gallons of waste per ton. In indirect ammonia-recovery plants the volume of waste amounts to about 90 gallons per ton.

The dilution of the still waste may be estimated from the analyses of ammoniacal liquor and the waste, the chloride determination being the most satisfactory.[80] For accuracy in such calculations, allowance should be made for salts introduced with the milk-of-lime.

The total ammonia in properly limed still waste usually amounts to a fraction

72 See pp. 142–3 of ref. 66.

73 Teed, F. C., *J. Soc. Chem. Ind.*, **4**, 709–10 (1885). Schrieb, H., *Z. angew. Chem.*, **2**, 211–3 (1889).

74 Sperr, F. W., Jr., U. S. Pat. 1,838,587 (1931).

75 Ragatz, K., and Spees, J. M., *Gas Age-Record*, **60**, 953–5, 962 (1927). Nishida, K., and Nakamura, S., *Rept. Central Lab., S. Manchuria Ry. Co.*, **1929**, 37–9; *Chem. Abs.*, **25**, 1952 (1931).

76 See pp. 1341–2 of ref. 67.

77 See p. 54 of ref. 11.

78 See p. 649 of ref. 2 and p. 15 of ref. 11.

79 See ref. 12.

80 Shaw, J. A., private communication, 1940.

TABLE XVII

Analyses of Ammoniacal Liquors and the Still Wastes Therefrom

Type of carbonizing operation	Coke Ovens [81]		Vertical Retorts	
Plant	A	B	A [82]	B [83]
Weak liquor composition, grams per liter				
NH₃, total	6.54	7.06	14.5	13.3
free	3.35	......	9.0	10.0
fixed	3.19	......	5.5	3.3
Sulfide as H₂S	.....	0.138	1.9	1.5
Carbonate as CO₂	.....	0.81		
Cyanide as HCN	.....	......	0.12	0.05
Thiosulfate as H₂S₂O₃	.....	......	0.46	1.78
Thiocyanates as HCNS	.....	......	1.22	2.03
Phenols as C₆H₅OH	.....	......	3.55	3.5
Oxygen absorption (4-hr test), ppm	.....	......	....	16,500
Recovery of fixed ammonia			Limed	Unlimed
Waste composition, grams per liter				
NH₃, total	0.041	0.0034	....	3.1
free	.....	0.0034	....	0.1
fixed	.....	......	....	3.0
Alkalinity as CaO	1.57	1.44	3.6	...
Sulfide as H₂S	.....	0.075	....	Trace
Carbonate as CO₂ .	.....	0.37	....	...
Thiosulfate as H₂S₂O₃	.....	......	0.21	1.60
Thiocyanate as HCNS	.....	......	0.54	1.83
Phenols as C₆H₅OH	.....	......	1.8	1.7
Oxygen absorption (4-hr test), ppm	.....	......	5,800	10,080

of a gram per liter. All fixed ammonium salts are converted to the corresponding calcium compounds, the chloride, sulfate, thiosulfate, and thiocyanate. Any carbon dioxide or hydrogen sulfide not removed in the free still is present as its calcium salt, and in addition there is an excess of lime, often amounting to approximately 1 gram per liter.

Some of the organic matter present in the original liquor is left in the still waste, but the total concentration is greatly reduced and its physical condition altered. As the lighter constituents are removed in the steam, much of the organic matter left tends to coagulate into masses of relatively low fluidity at 100° C, which upon cooling to room temperature are brittle solids.[80]

Analyses of several ammoniacal liquors and the still wastes produced therefrom are shown in Table XVII.

The waste liquor is generally discharged into baffled sumps. Here solid matter settles out, and the liquor cools. Accumulations of sediment are removed from the sumps by bypassing them periodically for cleaning.

PRODUCTION OF AMMONIUM SULFATE BY THE SEMI-DIRECT PROCESS

The stills which have just been described are used with the semi-direct process. The

81 Private communications, 1919–23.

82 Bailey, T. L., *Ann. Rept. Alkali, &c., Works,* 64, 34 (1928).

83 See pp. 9 and 17 of ref. 11.

vapors from these stills are cooled in a dephlegmator to reduce their content of water and then returned to the gas before the ammonium sulfate saturators.

The steam consumption for stripping ammoniacal liquor is between 2 and 3 pounds per gallon of liquor.[84] The quantity depends on the temperature of the liquor feed, the concentration of ammonia in the feed, the efficiency and size of the still itself, and the amount of reflux from the dephlegmator. Calculations have been made by Krieger [85] for the total steam consumption involved in ammonia recovery by the semi-direct, indirect, and Otto direct processes, including that consumed in compressing the gas for passage through the saturators.

PRODUCTION OF AMMONIUM SULFATE BY THE INDIRECT PROCESS

In the indirect process for the production of ammonium sulfate, the vapors from the dephlegmator are conducted into a bath of dilute sulfuric acid saturated with ammonium sulfate. Figure 6 shows a typical saturator, a lead-lined vessel to which the ammonia is admitted through the distributor or "cracker" pipe. Acid is added continuously to the bath in proportions sufficient to maintain 7–8 percent of free sulfuric acid.[86] As the sulfate is precipitated, it is withdrawn from the bottom of the bath by means of an air or steam ejector. The operation is similar to that of a semi-direct saturator.

The reaction is so strongly exothermic that the bath boils. Water is evaporated and leaves with the unabsorbed gases which accompanied the ammonia vapor from the still. Where escape of these gases into the

atmosphere will prove objectionable they must be purified. They are first cooled in condensers. The cooled gases from the condenser may be treated for removal of the hydrogen sulfide. Parrish [87] mentioned burning the gases to sulfur dioxide, which is used for the production of sulfuric acid or neutralized with limestone; burning to sulfur in a Claus kiln; and purification with iron oxide. Typical analyses of the condensates thus produced in horizontal- and vertical-retort plants are shown in Table XVIII.[88]

TABLE XVIII

ANALYSES OF CONDENSED VAPORS FROM INDIRECT SATURATORS [88]

Retorts	Horizontal		Vertical
Collected	Hot	Cold	
Temperature, °C	88	48	63
Analysis, grams per liter			
Cyanide as HCN	0.02	0.15	0.25
Sulfide as H_2S	0.02	0.20	0.50
Phenols as C_6H_5OH	5.52	8.07	7.60
Oxygen absorption, ppm	10,300	16,400	15,400

The condensate is usually mixed with the ammoniacal liquor or still waste, and both are disposed of together. The volume of the condensate may be taken as 10 to 15 percent of the volume of the mixture.[78, 84]

PRODUCTION OF CONCENTRATED AMMONIA LIQUOR

In the United States most of the ammonia produced in coke-oven plants is recovered as ammonium sulfate, but a portion is used for the production of concentrated ammonia liquors. During 1941 a little over 14 percent (62,777,031 pounds)

[84] See pp. 643 and 649 of ref. 2 and pp. 87–8 of ref. 11.

[85] Krieger, A., *Gas- u. Wasserfach*, **65**, 17–20 (1921).

[86] Private communication, 1926.

[87] See Chapter 14 of ref. 66.

[88] Bailey, T. L., *Ann. Rept. Alkali, &c., Works*, **61**, 14–5 (1925).
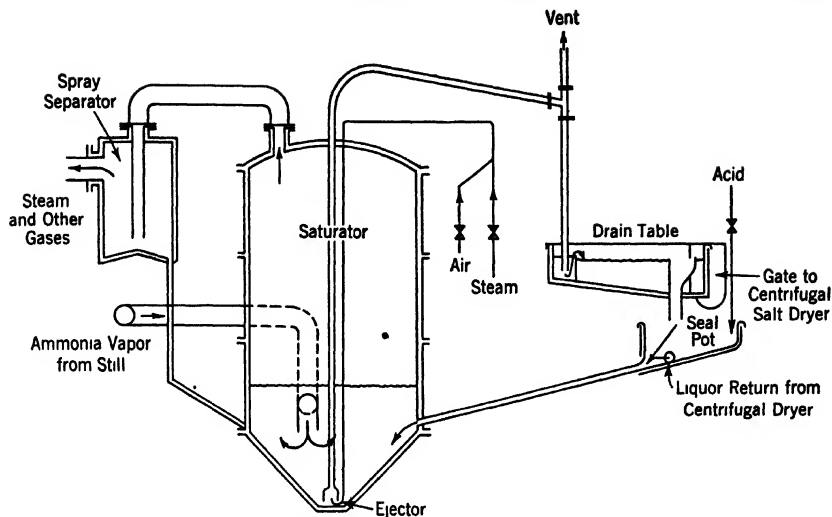
FIG. 6. Saturator for the production of ammonium sulfate by the indirect process.

was recovered as liquor.[89] There are two main types of concentrated liquors, crude and pure. The crude is usually the more dilute, the ammonia concentration ranging from 15 to 25 percent. The pure liquors usually run from 25 to 30 percent by weight ammonia.

Crude Ammonia Liquors. Crude ammonia liquor is usually a solution in condensed steam of the ammonia and many of the other compounds which were distilled from the weak liquor. There are two types: (1) liquors in which no removal of acidic gases is attempted, in which all the ammonia may be combined as carbonate and sulfide; (2) liquors in the production of which a partial removal of the acidic gases is effected. The former may be produced simply by adding to the ordinary ammonia still equipment for condensing

the mixture of vapors leaving the dephlegmator. The temperature of the dephlegmator is regulated to give a mixture of vapors with the composition of the liquor desired. A simple still designed for the production of such a crude liquor is outlined in Fig. 7.

The absorption of ammonia to produce a crude liquor of this type has been discussed by Key.[90] As the vapors are cooled in the condenser, water begins to separate, but the concentration of ammonia in the first condensate is much less than that in the final product. The condensate in its passage through the condenser is cooled further and absorbs more ammonia, together with other gases. The chief factors governing the rate of absorption of the ammonia, apart from the velocity constant

89 Ridgway, R. H., De Carlo, J. A., and Otero, M. M., "Coke and Byproducts," preprint from *Minerals Yearbook, Review of 1941*, U. S. Bur. Mines, p. 54.

90 See pp. 116–8 of ref. 11. Key, A., and Etheridge, W., *Inst. Gas Engrs., Copyright Pub.*, No. 168/57 (1937), 65 pp.; *Gas J.*, **220**, 511, 513–6, 659–61 (1937); *Gas World*, **107**, 454–7, 546–7 (1937); *Chem. Abs.*, **32**, 6434 (1938).

for the specific reaction, are (1) the ammonia concentration in the gaseous phase, (2) the concentration of uncombined ammonia in the solution, and (3) the temperature. Obviously, at a given temperature the ammonia absorption will at first

carbon dioxide concentration of the gas, (2) by the concentration of the uncombined ammonia in the solution, and (3) by the temperature. The carbon dioxide combines with the ammonia to form ammonium carbonate, so that the higher the concen-
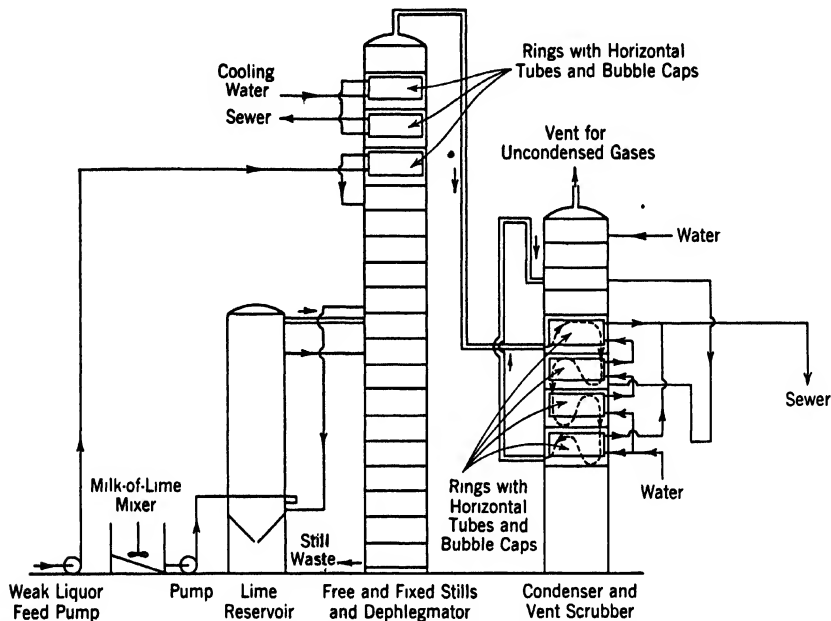
FIG. 7. Still for the production of crude ammonia liquor.

be high, but will decrease as the ammonia concentration of the solution increases and that of the gas decreases. Complete absorption of ammonia by the liquor is difficult, so that sometimes a supplementary scrubber fed by water or a little liquor is provided, in which the ammonia otherwise lost is recovered.

Carbon dioxide is not absorbed so readily by the condensate as ammonia is. In addition to the velocity constant for the absorption reaction, the rate of absorption of the carbon dioxide is controlled (1) by the

tration of the ammonia the higher will be the rate of absorption of the carbon dioxide. At a given temperature the absorption of carbon dioxide will at first be slow, because the ammonia content of the solution is low; it will then increase as the ammonia concentration increases and will finally fall off as absorption of the ammonia declines.

In the simple types of concentrated liquor plant the ratio of ammonia to carbon dioxide will not be much greater than that in the original liquor. The same will

be true for the ratio of ammonia to hydrogen sulfide. According to Key a concentrated liquor with 15 percent ammonia will contain about 18 percent carbon dioxide and 2 percent hydrogen sulfide. Terres and Weiser [8] have determined partial and total pressures of solutions containing ammonia and carbon dioxide for use in ammonia concentration.

Crystallization of Salts from Concentrated Liquor. When a concentrated liquor prepared by the simple distillation of weak ammoniacal liquor contains more than 18 percent ammonia, crystallization of salts may occur in the condensing equipment or storage tanks. The composition of the crystals has been studied by Key.[91] They may consist of ammonium bicarbonate, ammonium carbonate, or a double salt corresponding to the formula $2NH_4HCO_3 \cdot (NH_4)_2CO_3$, depending on the composition of the liquor. In addition, particularly with liquors which deposit crystals of the normal carbonate, ammonium carbamate ($NH_2CO_2NH_4$) is present in solution. Ammonium carbonate is, in fact, produced from and converted into ammonium carbamate by a reversible reaction. At air temperature, the carbonate-carbamate reaction is very slow and takes days or weeks to reach equilibrium. Liquors of the same apparent composition may thus crystallize or not crystallize according to the relative concentrations of carbonate and carbamate. Since the equilibrium appears usually to be displaced, if at all, towards the carbamate side, it is more likely that liquors will remain liquid than that they will crystallize.

The influence of hydrogen sulfide on these concentrations is not accurately known, but its addition does reduce the carbon dioxide content of the liquor in equilibrium with the crystals. As a rough approximation 1 percent of hydrogen sulfide can be taken as replacing 0.5 percent of carbon dioxide in equilibrium mixtures.

Crystallization temperatures for concentrated liquors prepared in the laboratory have been determined by Thorne.[92] The ammonia and carbon dioxide concentrations ranged from 16 to 20 and 11 to 19 percent, respectively, and hydrogen sulfide additions amounting to 3, 6, and 9 percent were made to the liquor.

Partial Decarbonation of Crude, Concentrated Liquors. Studies made on the composition of concentrated gas liquors containing ammonia and carbon dioxide in equilibrium with a solid phase [91] showed that, in liquors containing more than 15.8 percent ammonia by weight at 10° C, the ratio of ammonia to carbon dioxide must be greatly increased over that of the weak liquor in order to avoid deposition of crystals. Reduction in the carbon dioxide content of the concentrated liquor therefore becomes necessary. This can be done in one of two ways: either by modifying the conditions of condensation of the liquor so as not to dissolve carbon dioxide, or by expelling carbon dioxide from the weak liquor before distillation.

The second method is the one almost exclusively used. The preheated weak liquor is introduced near the top of a decarbonating column, which is usually of the bubble-plate type. Here the carbonates are dissociated by the carefully controlled application of steam, and the vapors evolved ascend in countercurrent flow to the stream of liquor.

The details of apparatus for partial decarbonation of the liquor have varied in different types of plants. In one plant,[93] a

[91] See pp. 118–21 of ref. 11. Key, A., and Etheridge, W., ref. 90.

[92] Thorne, W. F., *Gas J.*, **216**, 903–4 (1937).
[93] Wilton, T. O., Brit. Pat. 428,065 (1935). Frahm, *Gas- u. Wasserfach*, **70**, 482–4 (1927).

portion of the carbon dioxide was removed in a small multistage still through which a strictly limited amount of steam passed. Preheated weak liquor was fed into this still at a point below the top. Some carbon dioxide and a little ammonia were removed from the liquor by the steam, but escape of ammonia was prevented by the introduction of a stream of cold, weak liquor to the top sections of the column. The decarbonated liquor then flowed to the ordinary ammonia still.

Still[94] placed the decarbonating column on top of the free still. A portion of the steam passed from the free still up through the decarbonating column and drove the carbon dioxide out of the liquor. Any ammonia accompanying the carbon dioxide was reabsorbed by the stream of weak liquor entering at the top of the decarbonating section.

In another type of decarbonater,[95] preheated weak liquor together with a certain amount of steam was introduced into the decarbonator, which consisted of a splash chamber surmounted by a reflux system. Carbon dioxide and some ammonia were removed in the splash chamber; part of the ammonia was retained by the cold liquor flowing down the reflux sections, and the rest was extracted in an extra scrubber. In tests in an English plant,[90] the operation of a decarbonator of this type increased the concentration of the ammonia in the product by 20 to 30 grams per liter without causing crystallization troubles. The efficiency of decarbonation varied with the temperature in the decarbonator. It increased from 12 percent at 82° C to 30 percent at 90° C. Approximately 50 percent of the hydrogen sulfide was removed

at the same time. The gases, after passing through a scrubber for recovery of the ammonia, were desulfurized in an oxide box, and the carbon dioxide escaped to the air.

Practically complete decarbonation of ammoniacal liquor with a negligible loss of ammonia was effected, according to Wyld,[96] simply by preheating the liquor and then spraying into an empty column under a 25-pound pressure, no steam being used. Since the preheating was done with waste heat the arrangement was economical of steam.

In an apparatus designed by C. Otto & Co.,[97] the crude ammonia liquor was preheated in a heat exchanger forming the lower part of the apparatus. It then entered the upper liquor space of the column, in which it was heated by direct steam to 90–100° C. Here the greater portions of carbon dioxide and hydrogen sulfide were expelled, and the liquor flowed down through the heat exchanger and left the column for the regular still. By using a tall liquor space a pressure of 14 inches of mercury was maintained in the apparatus, which permitted the application of a higher temperature for dissociation. The waste gases from the decarbonator were generally returned to the coke-oven gas.

Complete removal of carbon dioxide in the decarbonator is difficult and sometimes would be undesirable because the concentrated product would contain largely ammonium hydroxide. The higher ammonia vapor pressure of the hydroxide tends to increase the loss of ammonia and makes it harder to handle than solutions of the salts.

The second method for increasing the ratio of ammonia to carbon dioxide is effective within certain limits. The efficiency

94 Still, C., Ger. Pats. 302,195 (1917), 351,633 (1922).

95 Parrish, P., Kitchen, W. T., and Burns, W. L., Brit. Pat. 449,347 (1936).

96 Wyld, W., Brit. Pat. 25,716 (1910).

97 See pp. 637–8 of ref. 2.

of ammonia solution in the condensate from the still condensers is decreased by increasing the throughput of the plant. Some ammonia and carbon dioxide leave the condensers, but the uncondensed ammonia is recovered by washing the escaping gases with the weak liquor which enters the still. The concentration of the product is not affected, and no appreciable increase in the steam to the still occurs.[98] The ratio of ammonia to hydrogen sulfide in concentrated liquor is approximately the same as in the still gases, so that a partial separation of these two substances by controlling the conditions of condensation is impossible.

In most of the recent British plants for production of concentrated ammonia liquor, only the free ammonia is recovered,[98] and the fixed salts are discharged in the unlimed liquor from the plant. When fixed ammonia is driven off from a liquor, it is not accompanied by hydrogen sulfide or carbon dioxide. Hence, by addition of the gases from the fixed still to those from the free still, the ratio of ammonia to carbon dioxide is increased and danger of crystallization is reduced.

Old equipment available around a plant has often been satisfactorily adapted for the preparation of crude concentrated liquors.[99] Stills have been described in which the free ammonia alone was utilized for the production of crude, concentrated liquor.[100] Douglas [101] withdrew a portion of the vapor from the liming chamber of an ammonia still and passed it through first a reflux condenser and then a condenser to produce concentrated ammonium hydroxide solution.

A process for separating the acidic gases and the ammonia distilled from an ammoniacal liquor has been patented by Koppers.[102] He selectively absorbed the ammonia in a concentrated solution of ammonium thiocyanate, which does not dissolve the hydrogen sulfide and carbon dioxide.

Analyses. Analyses of a crude concentrated liquor, the weak liquor from which it was made, and the still waste are shown

98 See Chap. 13 of ref. 11. Key, A., and Etheridge, W., in ref. 90.

99 Shewring, F., *Gas World,* **64,** 490–1 (1916). Greaves, W., *Gas J.,* **141,** 398 (1918) ; *Gas World,* **68,** No. 1754, Coking Sect., 13–4 (1918).
100 Unger, J. S., *Gas Age,* **36,** 301 (1915) ; *J. Gas Lighting,* **132,** 144 (1916). Raschig, F., Ger. Pat. 420,498 (1925).
101 Douglas, R. P., Brit. Pat. 161,244 (1919).
102 H. Koppers G.m.b.H., Ger. Pat. 661,881 (1938).

TABLE XIX

Analyses of Liquors from Concentrated Gas Liquor Plant [90]

	Liquor to Still	Still Waste	Concentrated Liquor
		grams per liter	
Ammonia			
total	26.39	5.48	219
free	19.90	0.39	219
fixed	6.49	5.09	.....
Sulfide as H_2S	2.21	....	19.3
Thiosulfate as $H_2S_2O_3$	2.44	2.14	.....
Thiocyanate as HCNS	2.47	1.57	.....
Phenols as C_6H_5OH	3.46	2.66	4.28
		parts per million	
Oxygen absorption (4 hr at 27° C)	17,880	11,820	39,110

in Table XIX.[90] Although there are discrepancies between the concentrations of the compounds in the products and the original liquor, the analyses will serve to indicate possible results.

The analysis of a crude liquor from an American plant has been reported by Stone, Table XX.[103]

TABLE XX

Analysis of Crude Ammonia Liquor [103]

Specific gravity	1.1055
Ammonia, total, percent	22.47
free, percent	22.20
Pyridine, grams per liter	2.79
Sulfides as H_2S, grams per liter	53.3
Organic number, cc $N/50$ $KMnO_4$	
per liter	103,300

A large number of samples of gas liquor from different plants were examined by Colman and Yeoman.[104] The compounds present in appreciable quantities were found in the following concentration ranges: ammonia, 25 percent; hydrogen sulfide, 0 to 3.1 percent; carbon dioxide, zero to small amounts; phenols (in a few samples), 1.1 to 3.7 grams per liter; pyridine bases, 2.6 grams per liter average; ammonium thiosulfate, 0.8 to 2.5 grams per liter; and cyanogen compounds, 0.245 gram per liter in gasworks liquors and 1.080 grams per liter in coke-oven liquors.

The relationship between the density at 15° C and the composition of concentrated gas liquors may be calculated by means of the equation: $d = 1 - 0.0004 \, NH_3 + 0.00094 \, CO_2 + 0.0005 \, H_2S$. The concentrations are expressed in grams per liter of liquor.[105]

Organic Matter. Organic matter, distilled from the weak liquor, including phenols, bases, and neutral oils, will also be present in the concentrated liquor. The solubility of the phenols in a distillate from an ammoniacal liquor is smaller than it is in water;[90] consequently a portion may separate as an oil on the surface of the concentrated liquor. Thus, although the phenol content of the total condensate may be 4 to 6 grams per liter, the actual concentration in the aqueous portion may not exceed 3 grams per liter. The quantity of oil separating can be of the order of 0.5 gallon per ton of concentrated liquor.

The approximate composition of the oily layer which formed on the top of the liquor at one plant has been reported by Philip:[106] pyridine bases, 22.5 percent; phenol, 39.5 percent; distillation: first drop 88° C, 10 percent at 187° C, 80 percent at 220° C, dry at 270° C.

Steam Consumption. The steam consumption depends largely on the strength of the weak liquor to the still, and also on the use of a decarbonator. The effect of these factors on the steam consumption of a still in which the liquor was not limed to recover fixed ammonia is shown in Table XXI.[105] Although the pounds of steam per gallon increased, the total steam consumed in the plant decreased as the ammonia concentration of the weak liquor increased. With recovery of all the ammonia, approximately 3 pounds of steam per gallon of weak liquor distilled has been reported.[107] Steam figures reported by Levin[108] amount to 2.5 pounds per gallon

103 Stone, C. H., *Proc. Am. Gas Assoc.*, **1923**, 1159–61.

104 Colman, H. G., and Yeoman, E. W., *J. Soc. Chem. Ind.*, **37**, 319-24T (1918); *Gas J.*, **144**, 567–8 (1919).

105 See pp. 127 and 137 in ref. 11. Key, A., and Etheridge, W., in ref. 90.

106 Philip, R. J., *Gas J.*, **199**, 645–8 (1932); *Gas World*, **97**, 245–8 (1933).

107 Terres, E., *J. Gasbeleucht.*, **60**, 399, 409 (1917). Terres, E., and Weiser, H., *ibid.*, **63**, 705–12 (1920). Mezger, R., and Bayer, T., *Gas- u. Wasserfach*, **68**, 651, 671 (1925). Lenze, F., and Rettenmaier, A., *ibid.*, **69**, 689 (1926).

108 Levin, Sh. M., *Coke & Chem. (U.S.S.R.)*,

TABLE XXI

RELATION OF WEAK LIQUOR STRENGTH AND
STEAM CONSUMPTION [105]

Free ammonia in weak liquor to still, grams per liter	7.5	15.	30.
Steam used, pounds per gallon of liquor			
Without decarbonator	1.42	1.83	2.66
With decarbonator	1.78	2.22	3.08

(Note: Steam has been converted from pounds
per 100 pounds of liquor in the original
work on the assumption that specific
gravity of the liquor is 1.)

of 1 percent ammonia liquor to the still.
The average steam consumption for the
distillation of liquor to produce ammonium
sulfate has been reported by Chevalet [109] to
be about 1.1 pounds per gallon.

The use of towers filled with Raschig
rings instead of the usual cast-iron column
sections increased the thermal efficiency of
ammonia concentration, according to Dommer.[110] When heat exchangers and preheaters were employed, the steam consumption was equivalent to 1.25 pounds
per gallon of weak liquor containing 1 percent ammonia.

The economic aspects of liquor concentration have been discussed by Parrish.[111]
He concluded that the process using partial
decarbonation is the most economical, flexible, and generally applicable. He recommended the production of concentrated liquors for utilization at central chemical
works in the production of ammonium sulfate, ammonium phosphate, nitric acid, and
other nitrogenous fertilizers.

After analyzing costs for the production
of concentration liquor, including cases in
which the fixed ammonia was discarded,
Bishop [112] concluded that cost of steam
and lime largely determines whether it is
economical to recover the fixed ammonia.

PURE AMMONIA LIQUORS

Aqua ammonia containing usually between 26 and 28 percent ammonia is produced with very small amounts of impurities. An analysis of a typical B grade liquor has been published by Perley and
White,[113] Table XXII.

TABLE XXII

ANALYSIS OF A PURE AMMONIA LIQUOR [113]

Ammonia	29.5	percent
Naphthalene	0.009	percent
Soluble tar	0.037	percent
Carbon dioxide	0.06	gram per liter
Hydrogen sulfide	Nil	
Pyridine	0.11	gram per liter

In a plant for the production of pure,
concentrated liquor the weak liquor is first
decarbonated. The ammonia and the remainder of the volatile impurities are then
distilled off in the standard free and fixed
ammonia stills. From the mixture of vapors
the acidic gases, hydrogen sulfide, carbon
dioxide, and hydrogen cyanide, may be
separated by absorbing them in a solution
of an inorganic base. Although any of the
inorganic alkalies can be used, ammonia
itself is usually the best.

The washing operation can be carried
out in a bubble plate column, made up of
cast-iron sections provided with cooling
coils to remove the heat of solution of the
gases and to maintain the proper temperature. The cooling of the vapors and their

1938, No. 11, 48; Khim. Rep. Zhur., 2, No. 4,
116 (1939); Chem. Abs., 34, 1465 (1940).
109 Chevalet, M., Gas World, 60, 227 (1914).
110 Dommer, O., Z. kompr. fluss. Gase, 25,
82–3 (1926).
111 See Chapter 18 of ref. 66. Parrish, P.,
Chem. Age, 22, 573–6, 608–9 (1930); Inst. Gas
Engrs., Commun. 213 (1939), 72 pp.

112 Bishop, J., Gas World, 106, No. 2740,
Coking Sect., 13–20 (1937).
113 Perley, G. A., and White, W. P., Ind. Eng.
Chem., 21, 564–7 (1929).

intimate contact with the washing liquors also serve to condense organic impurities.

A process of this type was patented by Pennock [114] and his coworkers. The liquor was decarbonated and desulfurized, and a portion of the organic impurities was vaporized by heating in a decarbonating column. The ammonia in the vapors was reabsorbed by the incoming liquor in the top sections of the decarbonator. The partially purified liquor from the decarbonator was distilled in the usual free and fixed stills, and the waste liquor was discharged from the plant. The mixture of vapors from the still, consisting of steam and the balance of the impurities, was dephlegmated and then washed with a saturated solution of ammonia. The solution of free ammonium salts plus impurities which collected in the base of the washing column was withdrawn and vaporized in a separate vessel, and these vapors were returned to the decarbonating column. Here they came in contact with the incoming stream of cold feed; the ammonia was absorbed, but the impurities were permitted to escape. The purified ammonia vapors from the top of the washing column were absorbed in water to produce an ammonia liquor of the desired strength.

Stills employing a similar system have been described by Hilgenstock [115] and by Plantinga.[116] They differed slightly from the system of Pennock in that the solution of ammonia and impurities from the washing column was simply added to the weak liquor. Hilgenstock emphasized the necessity for careful control of the water which

is introduced into the washing column. The additions must be regulated to remove the impurities efficiently without returning too large a proportion of the ammonia to the liquor entering the still.

Hilgenstock [115] passed the gases from the washing column through a small caustic scrubber in order to remove unabsorbed traces of carbon dioxide before the final absorption in water. For the production of chemically pure ammonium hydroxide he also passed the ammonia vapor through filters of bone black and charcoal.

A plant using a different process has been described by Hebden.[117] The gases from the still were purified by passing through the following units: three air-cooled condensers, a caustic soda washer to remove carbon dioxide, a slaked lime purifier to remove the final hydrogen sulfide, an oil washer to remove small amounts of phenols, pyridine, and other organic compounds, and finally a coke tower to remove traces of oil. The purified ammonia was then absorbed to produce the pure liquor. Morgan [18] and Robinson and Gilliland [118] also have described such arrangements briefly.

The fixed ammonium salts alone have been utilized by Sperr [119] for the preparation of a pure ammonia liquor. The free ammonia and volatile acidic gases were first distilled off with steam. The liquor, substantially free from these impurities, was limed, and distilled separately with steam, and the vapors condensed. This concentrated liquor would still, however, be contaminated with appreciable amounts of organic matter, particularly the less volatile compounds from the weak liquor.

114 Pennock, J. D., Witherby, E. C., Blauvelt, W. H., Trump, E. N., and Tufts, C. G., U. S. Pats. 1,012,272-3 (1911).

115 Hilgenstock, R. W., Chem. Engr., 15, 195–201 (1912); Gas World, 57, 482–3 (1913); J. Gasbeleucht., 58, 115–17, 709–14 (1915); Am. Gas Light J., 103, 241–3 (1916).

116 Plantinga, P., J. Gas Lighting, 133, 262–3 (1916).

117 Hebden, G. A., Gas J., 140, 609–10 (1917).

118 Robinson, C. S., and Gilliland, E. R., The Elements of Fractional Distillation, 3rd ed., McGraw-Hill Book Co., New York, 1939, Chapter IX.

119 Sperr, F. W., Jr., U. S. Pat. 1,928,510 (1933).

Ammonia evaporates much more rapidly than water from solution, and care is therefore necessary in storage. In three days the ammonia contents of three solutions of ammonium hydroxide decreased from 34.5, 25.7, and 22.7 percent to 6.2, 6.3, and 6.3 percent, respectively, while the loss of water amounted to 1 or 2 percent from each solution.[120]

PRODUCTION OF AMMONIUM BICARBONATE

Reports coming from Great Britain indicate that ammonium bicarbonate for use as a fertilizer in place of sulfate has been accorded serious attention. Ammonium bicarbonate has an important advantage over sulfate in that the cost of sulfuric acid is saved.[121] Experiments [121, 122] have demonstrated that ammonium bicarbonate, concentrated ammonia liquor, and ammonium sulfate, when properly applied, should have about the same fertilizing effects for the same weights of nitrogen applied. Ammonium bicarbonate is likely to lose considerable quantities of ammonia by volatilization when applied on the surface of the soil so as to be exposed to air currents. This loss may be prevented by applying the bicarbonate beneath the surface of the soil, for instance, by sowing with drills. The presence of carbon dioxide in the bicarbonate should prove an advantage, because tests have shown that carbon dioxide in the soil has a favorable influence on plant growth.[121, 123]

Although ammonium bicarbonate has been produced at one German plant with complete satisfaction for a number of years, the process [124] has not been introduced at other plants to any extent. For production of ammonium bicarbonate, the weak liquor is converted into crude, concentrated liquor. Since insufficient carbon dioxide is present to convert all the ammonia into ammonium bicarbonate, carbon dioxide is added. The ammonium bicarbonate is precipitated in the form of crystals, which may be easily filtered or separated in centrifugal driers.[125] Ammonium carbonate is not precipitated, and ammonium sulfide is decomposed by the carbon dioxide. The reaction is exothermic, and cooling is necessary. A small scrubber for removing traces of ammonia contained in the waste gases is needed.

Carbon dioxide is obtained from the coke-oven gas itself, or from outside sources. Coke-oven gas was used by Still.[126] He washed the carbon dioxide out of crude gas by means of a special liquor containing ammonium hydroxide, and subsequently vaporized it in a concentrated form by heating the liquor to 90° C or higher under special conditions. The revivified liquor was cooled and returned to the gas washers. The handling of two stills and two liquors was a disadvantage of this

[120] Auerbach, E. B., and Millbradt, L., *Z. angew. Chem.*, **34**, Aufsatzteil 95–7 (1921).

[121] Gluud, W., *Ber. Ges. Kohlentech.*, **1**, 127,-320 (1923); *Chem.-Ztg.*, **46**, 693–7, 715–17 (1922). See also pp. 644–7 of ref. 2.

[122] Tacke, *Mitt. Förderung Moorkultuur*, **49**, 227, 243, 337 (1921); *Chem. Zentr.*, **93**, I, 1211 (1922). Gluud, W., *Fertiliser, Feeding Stuffs Farm Supplies J.*, **7**, 197 (1922). Haselhoff, E., Liehr, O., and Fluhrer, K., *Landw. Vers. Sta.*, **100**, 37–58 (1922); *Chem. Abs.*, **17**, 2162 (1923). Lemmermann, O., and Eckl, K., *Z. Pflanzernähr. Düngung*, **2B**, 98–109 (1923); *Chem. Abs.*, **18**, 2936 (1924). *Inst. Gas Engrs., Commun.* 142 (1936), 87 pp.; *Trans. Inst. Gas Engrs.*, **86**, 265 (1936–37). See also pp. 81–3 of ref. 11.

[123] Riedel, F., *Stahl u. Eisen*, **39**, 1497–1506 (1919); *Chem.-Ztg.*, **45**, 157–8, 829–30 (1921). Reman, E., *Chem.-Ztg.*, **43**, 449–51, 469–72, 489–91, 509–12, 524–5 (1919); U. S. Pat. 1,611,072 (1926). Fischer, F., Ger. Pat. 368,222 (1922).

[124] Schreiber, F., *Die Industrie der Steinkohlenveredelung*, F. Vieweg & Sohn, Braunschweig, 1923, 192 pp., especially p. 180. Thau, A., *Gas u. Wasserfach*, **68**, 799–805 (1925). Foxwell, G. E., *Ind. Chemist*, **9**, 208–11 (1933).

[125] Gluud, W., *Ber. Ges. Kohlentechnik*, **1**, 143 (1923). See also p. 645 of ref. 2. Thau, A., *Gas- u. Wasserfach*, **68**, 799–805 (1925).

[126] Still, C., Ger. Pat. 362,378 (1922).

process, but removal of carbon dioxide from the coke-oven gas was an advantage, because the calorific value was thereby increased.

In the MacLaurin process,[127] the extra carbon dioxide was supplied in the form of flue gases, introduced either hot at the bottom of the still or cold at the top. The mixture of gases from the still was cooled and then bubbled through the condensate in a crystallizer where the bicarbonate was deposited. Unless the flue gases were freed from sulfur dioxide, the product contained a small percentage of ammonium sulfite or sulfate.

The carbon dioxide in the Lewis[128] process was added to the vapors from the ammonia still in the form of waste gases from lime or Portland-cement kilns or furnaces. The mixture of gases, when cool, deposited ammonium carbamate, which was converted into ammonium bicarbonate by the addition of water and a further quantity of carbon dioxide.

Parrish[129] described processes in which concentrated liquor was used. In one the liquor was distilled and the carbon dioxide in a concentrated form (flue gases) added to the vapors. The mixture of gases was then cooled and ammonium bicarbonate precipitated. The conversion of ammonia in the concentrated liquor could also be secured by introducing the carbon dioxide into a tower down which the liquor trickled. This process, tried out on an experimental scale, was said to work without difficulty.[130]

Carbon dioxide has been obtained by distilling the ammonium liquor in contact with limestone or similar carbonates.[131]

The ammonium chloride decomposes the limestone with the evolution of ammonia and carbon dioxide. Wächter[132] introduced a stream of ammonia liquor directly into a lime kiln.

The carbon dioxide requirements for precipitation of ammonium bicarbonate from ammonia liquors were examined by Fischer and Hilpert.[133] For precipitation of 55 percent of the ammonia from a 10 to 25 percent solution with a gas mixture consisting of 1 part of carbon dioxide plus 4 of air, about 10 times the theoretical requirement of carbon dioxide was necessary. Much ammonia was carried away with the gases.

Ammonium bicarbonate may be recovered directly in the solid form from the coke-oven gas itself if the concentrations of the reacting materials are brought to the conditions for equilibrium as expressed by the equation:[134]

$$NH_3 + CO_2 + H_2O \rightleftharpoons NH_4HCO_3$$

$$K = \frac{(NH_3)(CO_2)(H_2O)}{(NH_4HCO_3)}$$

Since the composition of a saturated solution of ammonium bicarbonate is fixed, it may be included in the equilibrium constant K, together with the concentration of the water vapor in the gas. The equation then becomes $K' = pNH_3 \times pCO_2$, where p stands for the partial pressure of the two gases, respectively.

When the concentration of carbon dioxide is expressed as a volume percent, and that of the ammonia in terms of grains per 100 cubic feet, the value of K' is 984 at 20° C and 158 at 10° C. In crude gas from coke ovens or vertical retorts, this value

127 MacLaurin, R., Brit. Pat. 360,613 (1937).
128 Lewis, H. R., Brit. Pat. 14,618 (1895).
129 Parrish, P., Brit. Pat. 379,319 (1932).
130 See p. 106 of ref. 11.
131 Seidler, P., *Dinglers Polytech. J.*, **252**, 476–8 (1884); Ger. Pat. 26,633 (1884). Teed, F. C., *J. Soc. Chem. Ind.*, **4**, 709–10 (1885).

132 Wächter, P., Ger. Pat. 34,393 (1886).
133 Fischer, F., and Hilpert, S., *Ges. Abhandl. Kenntnis Kohle*, **1**, 291–2 (1917).
134 Hutchison, W. K., *J. Chem. Soc.*, **1931**, 410–2. See also pp. 106–7 of ref. 11.

ranges from 600 to 800, so that, by cooling the gas to about 10° C, solid ammonium bicarbonate would precipitate.

Ammonium bicarbonate can be recovered directly from the gas by building up the necessary concentrations of ammonia and carbon dioxide; according to Wilson,[135] cooled, tar-free gas was compressed to a pressure of 3 atmospheres and the ammonia from the ammonia still returned to it. After further removal of tar and oil, the compressed-gas mixture was washed with a saturated solution of ammonium bicarbonate. Solid salt separated from the liquor and was removed for drying. This process worked on a small scale without undue trouble, but the great drawback was compression of all the gas, together with the necessary cooling.

Key[136] attempted to produce the necessary equilibrium conditions for precipitation of ammonium bicarbonate by concentrating the carbon dioxide and ammonia in a portion of the gas stream. The ammoniacal liquor was distilled in the usual way, and the vapors from the dephlegmator containing carbon dioxide as well as the ammonia were introduced into a portion of the gas, the proportion of which depended on its carbon dioxide content. This gas, containing all the ammonia from the total gas plus sufficient carbon dioxide to combine with it, was then washed with a saturated solution of ammonium bicarbonate. Key concluded that operation of this process on a large scale would be difficult for two reasons: (1) the saturated bicarbonate solution would contain a large excess of ammonia, loss of which would be difficult

to prevent; and (2) dissipation of the heat of formation of ammonium bicarbonate without allowing the temperature of the solution to exceed 20° C would be difficult. He[137] therefore proposed scrubbing portions of the ammonia and carbon dioxide from the gas. This liquor was distilled in a sectional still. In the upper section the carbon dioxide together with sufficient ammonia for combination to bicarbonate was driven off and absorbed in a saturated bicarbonate solution. The free ammonia left in the liquor was then driven off in the lower section of the still and condensed to form a solution containing 5 to 10 percent ammonia. This liquor was used for scrubbing more carbon dioxide from the gas. The process has been worked in the laboratory.

Methods for the purification of the gases from an ammonia still to be used in the production of ammonium carbonate have been described. Raspe[188] used zinc carbonate or metallic oxides to remove hydrogen sulfide and organic matter. In addition to purifying the gases, Hilgenstock[139] resublimed the ammonium carbonate which he produced.

A method for producing ammonium carbonate was patented by Black and Evans.[140] Alcohols of low boiling point, such as ethanol or methanol, were added to ammoniacal liquor and the mixture distilled at temperatures below 100° C, preferably 80°. The distillate was condensed to pro-

[135] Wilson, W., Brit. Pat. 319,441 (1928); *Trans. Inst. Gas Engrs.*, **80**, 270 (1930–31).

[136] Institution of Gas Engineers and Key, A., Brit. Pat. 393,678 (1933). Key, A., and Eastwood, A. H., *Ins. Gas Engrs., Commun.* **77**, 44–54 (1933); *Trans. Inst. Gas Engrs.*, **83**, 175–82 (1933–4).

[137] Institution of Gas Engineers and Key, A., Brit. Pat. 455,648 (1936). Key, A., Etheridge, W., and Eastwood, A. H., *Inst. Gas Engrs., Commun.* **123**, 11 (1935); *Trans. Inst. Gas Engrs.*, **85**, 404 (1935–36); *Gas World*, **103**, 389–90, 423–4, 439–40 (1935); *Gas J.*, **212**, 476–82 (1935).

[138] Raspe, C., Ger. Pats. 70,977 (1893), 83,556 (1895).

[139] Hilgenstock, R. W., *Am. Gas Light J.*, **93**, 483 (1911).

[140] Black, A. G., and Evans, P., Fr. Pat. 800,-988 (1936); Ger. Pat. 658,900 (1938).

duce solid ammonium carbonate and a solvent for fats.

The volatility of ammonium bicarbonate is a disadvantage to its handling, but tests have shown that losses are largely eliminated when the salt is suitably packed.[141] Attempts have been made to counteract the volatility by addition of dehydrated salts, resins, paraffin and similar materials.[142]

The production of the bicarbonate in a coarsely granular form stable to storage has been claimed by a German inventor.[143] Carbon dioxide was led into a solution saturated with compounds of ammonia and carbon dioxide under such conditions that the amount of ammonium bicarbonate which separated from the solution was 8 to 24 grams per liter of solution per hour.

Contamination of the ammonium carbonate with lead could be avoided, Lennard[144] stated, by using aluminum for constructing the apparatus in which the sublimation and condensation were carried on.

Ammonia Distillation by Use of Fixed Gases. Gas, instead of steam, has been used to distil ammonia from liquor. The mixture of gas and ammonia from the still was returned to the main body of gas. Schuster[145] patented the use of a small stream of gas preheated at 100 to 400° C for stripping preheated liquor.

Wilton[146] added an alkali to the am-moniacal liquor and returned the solution to the hot gas main. The fixed salts were decomposed, and the ammonia was vaporized into the hot gases.

The Berlin-Anhaltische Maschinenbau A-G.[147] distilled the ammonia from the liquor by means of the waste gases from the retorts. The apparatus was arranged in the smoke flue of the stack, and the ammonia was discarded with the gases to the atmosphere.

MANUFACTURE OF AMMONIUM CHLORIDE

Ammonium chloride has been produced by concentrating ammoniacal liquors and crystallizing the salt. Owing to the low concentration of chloride in the liquor, the steam requirements are high unless waste heat can be utilized. In a number of instances, the liquor has been concentrated by recirculation through the collecting main in contact with the hot gases from the ovens, before final evaporation for the solid salt.

This method was used by Heimbach and Thompson.[148] The chloride concentration of the flushing liquor was built up by recirculation and evaporation in the mains to 5–15 percent. Liquor was withdrawn to maintain this concentration and sent to a double-effect evaporator made of 18-8 nickel-chromium stainless steel. The evaporator, of standard design with a vertical tube basket, was operated with parallel flow of steam and liquor. The second effect delivered crystallized salts, which could be purified by centrifuging and recrystallization.

Although analyses showed that this ammonium chloride was practically pure, it gave poor results when used in sheet gal-

[141] Gluud, W., *Ber. Ges. Kohlentechnik*, **1**, 127, 320 (1923). Foxwell, G. E., *Ind. Chemist*, **9**, 208–11 (1933).

[142] Österreichischer Verein, Ger. Pat. 313,327 (1919). Badische Anilin und Sodafabrik, Ger. Pats. 301,674, 310,055, 310,056 (1920), 333,671, 336,100 (1921). Welter, L., and Weindl, A., Ger. Pats. 332,114 (1920), 351,130 (1922).

[143] Bergwerksverband zur Verwertung von Schutzrechten der Kohlentechnik G.m.b.H., Ger. Pat. 664,070 (1938).

[144] Lennard, F., Brit. Pat. 5603 (1904).

[145] Schuster, N., U. S. Pat. 1,244,903 (1917); Brit. Pats. 6061 (1914), 12,220 (1918).

[146] Wilton, G., Brit. Pat. 23,043 (1908).

[147] Berlin-Anhaltische Maschinenbau A.-G., Ger. Pats. 204,858 (1907), 208,254 (1908).

[148] Heimbach, C. H., and Thompson, N. B., U. S. Pat. 2,179,183 (1939).

vanizing. The trouble was due to the presence of minute amounts of substances which were described as "ammonia salts of certain organic acids." A portion of these impurities was soluble in water and therefore could not be removed from the mother liquor by filtration before recrystallization. But upon heating the ammonium chloride in the galvanizing operation, the composition of the impurities was changed, and black, sticky substances were produced which stuck to the sheets and damaged the product.

These organic salts, of which the inventors said there were hundreds, were eliminated by washing the chloride with ethanol. The ammonium chloride from the evaporator was placed in the centrifugal drier, washed with water, then with a 50 percent solution of ethanol, and finally with water again to remove the alcohol. The chloride was finally redissolved to form an ammonium chloride solution saturated at 80° C. The heating of the solution rendered any residual impurity in the chloride insoluble. The solution was filtered and crystallized. The crystals were centrifuged, washed with water, and dried.

The mother liquor drained from the crystals was used to redissolve more alcohol-washed ammonium chloride. The alcohol was redistilled for further use.

Hacker and Lloyd [149] patented a process for concentrating ammonia liquor by circulating it through hot gases from the ovens until, on cooling without further evaporation, ammonium chloride crystallized out. Before crystallization the liquor was purified to remove tar and phenols.

In the retort house of the Partington Gas Works, Holton [150] recirculated the liquor until the concentration of ammonium chloride had built up to 14–18 percent. About 5 gallons of the concentrated liquor per ton of coal carbonized was withdrawn periodically for further evaporation and crystallization. The impure chloride was either recrystallized, or the concentrated liquor, before evaporation, was filtered through sawdust and activated carbon. The final salt was a pale pink and contained 98.3 percent ammonium chloride. An analysis of concentrated liquor withdrawn for evaporation is shown in Table XXIII.

TABLE XXIII

Concentrated Flushing Liquor to Be Evaporated for Ammonium Chloride [150]

Specific gravity at 15.5° C	1.08	
Ammonia		
fixed	87.6	grams per liter
free	1.0	gram per liter
Chloride as HCl	188.9	grams per liter
Sulfide as H_2S	0.06	gram per liter
Cyanide as HCN	0.16	gram per liter
Sulfocyanate as HCNS	0.4	gram per liter
Thiosulfate as $H_2S_2O_3$	1.41	grams per liter
Sulfate as H_2SO_4	0.8	gram per liter
Phenol as C_6H_5OH	7.5	grams per liter
Oxygen absorbed	18,200	parts per million

Recovery of ammonium chloride from recirculated liquor was described by Cobb and Key.[151] The tar acids in the liquor were "salted out" as the ammonium chloride concentration increased. This effect is illustrated by the analyses of three samples of liquor which had been shaken at 60° C with the same vertical retort tar, Table XXIV. By evaporation of a slightly acidified liquor, containing 12 percent ammonium chloride and having an oxygen absorption of 20,650 parts per million, to

149 Hacker, J. W., and Lloyd, T. C., U. S. Pat. 1,849,923 (1932).

150 Holton, A. L., *Gas Engr.*, 48, 882–5 (1931); *Gas J.*, 194, 790–801 (1931); *Gas World*, 94, 625, 735 (1931).

151 Cobb, J. W., and Key, A., *Gas J.*, 196, Suppl. Binding, 14–16, 409 (1931); *Gas World*, 95, 422–4, 466–9, 497 (1931).

Liquor	Phenol	Oxygen Absorption (difference figure representing higher tar acids)
	grams per liter	parts per million
Water	3.16	4,910
10 percent NH₄Cl	2.01	3,460
20 percent NH₄Cl	1.56	2,720

about one-third of the original volume and cooling, crystals were obtained which contained not more than 0.27 percent impurities of the higher tar acid type. The purity of chloride calculated from the ammonia content was 99.8 percent. The salt was slightly pink, the color becoming darker on exposure to the air. Recrystallization produced a greatly improved salt.

Ammonium thiocyanate and tarry matter may be removed from the chloride by washing with an organic solvent, such as pyridine, according to Key.[152]

The mother liquor from crystallization of ammonium chloride contained chiefly ammonium chloride, thiosulfate, and sulfate, according to Grossman.[153] This liquor may be worked up with lime in the still for recovery of the ammonia. Grossman treated the liquor with sufficient sulfuric acid to combine with the ammonia of the thiocyanate for the production of ammonium bisulfate. On heating the acid solution to 100° C, part of the thiocyanate was destroyed. Another part distilled over and reacted with limestone to produce calcium thiocyanate. Hydrochloric acid has been added to ammonium chloride liquors in order to decompose fixed salts other than the chloride, such as thio compounds.[154]

The production of ammonium chloride by the evaporation of the unlimed liquor from the free still has been reported by Thau.[155] A simple method for the production of ammonium chloride [156] is addition of hydrochloric acid to combine with all free ammonium compounds in the liquor, followed by concentration.

Ammonium chloride was produced from ammonia liquor by Dubosc and Henzey [157] by addition of a mixture of calcium and ferric chlorides. The sulfides and carbonates in the liquor were completely precipitated at the same time.

Smith [158] stated that white, "commercially" pure ammonium chloride crystals could be obtained from a crude solution by circulating the solution over steam pipes and then cooling and crystallizing.

A process was developed by Gluud,[159] in which ammonium chloride was produced from sodium chloride and ammonium bicarbonate. A saturated solution of sodium chloride was treated with ammonium bicarbonate (or with ammonia and carbon dioxide), which precipitated sodium bicarbonate. To the mother liquor from this precipitation was added sodium chloride, which precipitated ammonium chloride. Ammonium bicarbonate was again added to the second mother liquor, and the cycle of precipitations continued indefinitely.

Ger. Pat. 271,421 (1912). Jacobson, D. L., U. S. Pat. 1,831,864 (1931).

[155] Thau, A., Gas- u. Wasserfach, 68, 799–800 (1925).

[156] Hilgenstock, R. W., Gas World, 57, 482–3 (1912); Chem. Engr., 15, 195–201 (1912). Heineken, M., J. Gasbeleucht., 62, 30 (1919).

[157] Dubosc, A., and Henzey, J. Soc. Chem. Ind., 9, 614–5 (1890).

[158] Smith, T. B., and Simon-Carvés, Ltd., Brit. Pat. 234,933 (1924).

[159] Gluud, W., and Löpmann, B., Ber. Ges. Kohlentech., 3, 101 (1930); Z. angew. Chem., 43, 190–4 (1930); U. S. Pat. 1,710,636 (1929); Ger. Pats. 388,396 (1923), 394,578 (1924). Gesellschaft für Kohlentechnik m.b.H., Brit. Pats. 229,640 (1925), 243,677 (1926).

[152] See p. 67 of ref. 11.

[153] Grossman, J., J. Gas Lighting, 96, 526–8 (1907).

[154] Berlin-Anhaltische Maschinenbau A.-G.,

The solid products were centrifuged and washed. A plant of medium size using this process was operated successfully. Since pure ammonium bicarbonate and sodium chloride could be added, a high-quality product could be produced.

The size and shape of ammonium chloride crystals may be altered to suit the consumer's requirements by additions of very small quantities of other substances, such as chlorides of iron, manganese, copper, or nickel.[160]

Corrosion of equipment is a great problem at plants in which ammonium chloride is handled. Practically all metals which can be used commercially are seriously attacked. Everhart[161] reported that a nickel-chrome-molybdenum alloy was resistant to ammonium chloride liquors. Bacon[162] claimed that evaporation of ammonium chloride in the presence of free ammonia reduced the rate of corrosion, because dissociation of the chloride was reduced. Weber[163] found that the presence of zinc or cadmium ions reduced corrosion during evaporation and that a weak direct current also helped. Wood, particularly pitch pine, and stoneware were used by Hilgenstock[156] in a plant for the recovery of ammonium chloride.

Evaporators for concentration of ammonium chloride solutions were described by Brown.[164] Steel evaporators had cast-iron

tubes or were lined with lead or acid-proof brick and provided with extra-heavy copper or bronze tubes.

PRODUCTION OF AMMONIUM SULFATE BY USE OF STACK GASES, PICKLE LIQUOR, OR OTHER MEANS

Stack gases have been utilized to provide the sulfate for the production of ammonium sulfate. In the patents of Hodsman,[165] ammoniacal liquor was exposed to chimney gases containing sulfur dioxide. The sulfite which was formed was oxidized to sulfate, and at the same time a substantial portion of the liquor was evaporated. The product was either ammonium sulfate, a solid mixture of ammonium salts in which sulfate predominated, or a highly concentrated solution of the salts. Sperr[166] has described a similar process. The hydrogen sulfide in the gas was the source of the sulfate in a process developed by Wagner.[167] The gas was washed with a strong solution of sulfur dioxide which combined with the hydrogen sulfide to form complicated sulfur compounds. The solution was then combined with the ammonia liquor, heated, and oxidized with air to ammonium sulfate.

Ammonium sulfate has also been produced by use of pickle liquor. Into a solution of the iron sulfate, Sperr[168] passed ammonia vapor substantially free from acidic gases, such as the vapor from the fixed ammonia still. The iron hydrates which were formed were oxidized to the ferric compounds and separated from the ammonium sulfate solution.

Sierp[169] has described German processes

[160] Dubosc, A., *Bull. soc. ind Rouen*, **41**, 335 (1913); *Chem. Abs.*, **8**, 2988 (1914). Ehrlich, F., *Z. anorg. allgem. Chem.*, **203**, 26 (1931). Freitag, F., *Chem. Trade J.*, **87**, 477–9 (1930). I. G. Farbenindustrie A-G., Ger. Pat. **489,126** (1925); Brit. Pat. **481,129** (1938). Imperial Chemical Industries, Ltd., Fr. Pat. **689,040** (1930); Ger. Pat. **525,530** (1930); C. W. Bunn, U. S. Pat. **1,848,513** (1932).

[161] Everhart, J. L., *Chem. & Met. Eng.*, **39**, 88 (1932).

[162] Bacon, N. T., U. S. Pat. **1,416,772** (1922).

[163] Henkel et Cie and Weber, W., Brit. Pats. **196,585** (1923), **207,142** (1924).

[164] Brown, S. N., *Chem. Trade J.*, **74**, 123–4 (1924).

[165] Hodsman, H. J., and Taylor, A., Brit. Pats. **356,283, 360,574** (1932). Holmes, W. C., and Co., and Hodsman, H. J., Brit. Pat. **377,959** (1932).

[166] Sperr, F. W., Jr., Can. Pat. **336,145** (1933).

[167] Wagner, F. H., U. S. Pat. **1,020,168** (1912).

[168] Sperr, F. W., Jr., U. S. Pats. **1,983,320** (1934), **1,986,900** (1935).

[169] Sierp, F., *Stahl u. Eisen*, **58**, 491–7 (1938).

in which the ammonia from the stills has been treated with pickle liquor for the production of ammonium sulfate. Use of the waste acid from the benzol refining process has also been proposed. It is combined with the ammonia liquor to produce a concentrated solution of ammonium sulfate.[170]

PRODUCTION OF OTHER AMMONIUM SALTS

The preparation of fertilizers by the addition of phosphoric acid to ammonia liquor, evaporation of the solution, and crystallization of ammonium phosphate has been patented by Hansen.[171] By adding ammonia liquor to superphosphate, Bongiovanni[172] produced an ash-colored, almost odorless, nonhygroscopic fertilizer, free from cyanides and thiocyanates. Recovery of ammonium salts, including sulfide, thiosulfate, and thiocyanate, in crystalline form successively by evaporation and crystallization from the liquor was patented by Knapp.[173]

UTILIZATION OF AMMONIA LIQUOR

A number of industrial applications for weak ammoniacal liquors have been suggested, but none are known to be of commercial importance. The liquor has been used in place of dilute alkalies. Thus Chevalet[174] suggested adding ammoniacal liquor for the precipitation of lime salts from water prior to use of the water for gas washing or as feed water.

Simmer[175] patented the utilization of gas liquor as a source of nitrogen in fermentation processes. The liquor was acidified

and distilled to remove volatile impurities. It was then made slightly alkaline and filtered through active carbon.

The use of the aqueous liquor produced in the low-temperature coking of coal directly as a photographic developer has been patented by Fischer and colleagues.[176] Before its use the liquor was distilled until the phenolic odor disappeared.

The residual condensation products which are produced by the addition of aldehydes to the waste liquors, according to Bunge and Macura,[177] may be mixed with a binder such as linseed oil for the production of paints.

Jones and Bury[178] described the use of ammoniacal liquor as a frothing agent for separating finely divided coal or other carbonaceous material from water in which it was suspended. The froth contained the coal and the organic matter of the liquor. Froth flotation could also be utilized for separating suspended carbonaceous material from the liquor itself. Keith[179] described the removal of sulfides from gas liquors destined for hydrometallurgical use by the addition of zinc oxide. The zinc sulfide precipitate was separated. The utilization of purified waste liquors for washing coal was patented by Hinselmann.[180]

Still waste was added to the flue dust from blast furnaces by Marquard.[181] On aging of the mixture, a reaction occurred which caused the dust to bind together so

[170] Phoenix A-G. für Bergbau- u. Hüttenbetrieb., Ger. Pat. 289,162 (1914).

[171] Hansen, C. J., Brit. Pat. 342,318 (1929).

[172] Bongiovanni, C., *Staz. sper. agrar. ital.*, **52**, 521–3 (1919); *Chem. Abs.*, **15**, 3536 (1921).

[173] Knapp, W. R., U. S. Pat. 1,823,364 (1931).

[174] Chevalet, M., *Gas J.*, **163**, 735 (1928).

[175] Simmer, F., Ger. Pat. 524,981 (1927).

[176] Fischer, F., Schrader, H., and Tropsch, H., Ger. Pat. 374,005 (1922).

[177] Bunge, F. C., and Macura, H., Ger. Pat. 505,570 (1927); Brit. Pat. 326,112 (1929). Bunge, F. C., Fr. Pat. 676,871 (1929).

[178] Jones, F. B., and Bury, E., Brit. Pat. 165,-144 (1920); U. S. Pat. 1,388,868 (1922).

[179] Keith, E. W., U. S. Pat. 1,573,169 (1926).

[180] Hinselmann, G., Ger. Pat. 274,151 (1912).

[181] Marquard, F. F., U. S. Pat. 1,680,107 (1928).

that it could be recharged into the blast furnace without crumbling.

Ammoniacal liquors may sometimes be utilized in other processes around the coke or gas plant. Bailey has listed [182] the utilization of still wastes for washing gaseous products of combustion, use in coal washing, discharge onto waste spoil heaps, particularly those on fire, replacement of water in milk-of-lime mixers, and others.

THE USE OF AMMONIACAL LIQUOR AS A FERTILIZER

Good results have been secured by the use of ammoniacal liquors directly as a fertilizer. In 1922, Mews [183] stated that gasworks in Germany sold crude gas liquor containing 1.5 percent ammonia for agricultural purposes. When properly used, it did not harm plants and gave good results. In Belgium it was sold under the name of sulfocyanide of ammonia.[184]

Demolon [185] reported that the ammonia nitrogen was easily utilized. The thiocyanate disappeared slowly and with difficulty in soils. The ferrocyanides appeared to be stable, but the tarry substances were more or less toxic to plants, especially during germination. In discussing the studies of the Rothamsted station on the action of antiseptics on soil, Russell and Buddin [186] showed that protozoans which kept down the bacterial population could be eliminated by means of antiseptics. Among the antiseptics which gave good results were pyridine, phenol, cresols, and benzene and its homologs. After the addition of these antiseptics, the number of bacteria increased,

and the productiveness of the soil was raised. In tests on solutions containing between 1 and 5 percent ammonia, Beaumont and Larsinos [187] found that, as a carrier of fertilizer nitrogen, aqua ammonia was about 70 percent as effective as ammonium sulfate and sodium nitrate.

Ammoniacal liquors should be applied and plowed under about two weeks before seeding in order to avoid the toxic effects of phenols, hydrogen sulfide, thiocyanates, and cyanides on the plants, according to Mach.[188] Paturel [189] emphasized that the liquor will kill vegetation if applied directly, but, by contact with the soil, the harmful substances are converted into ammonium compounds and utilized by nitrifying bacteria. Methods of application, either directly to the soil or in admixture with manure, were described, and the optimum quantities to use on different crops were stated, on the basis of German experience. Gas liquor kills insects, larvae, weeds, and parasitic plants. This beneficial action was ascribed to the phenol.

The use of raw ammonia liquor containing about 1 percent nitrogen on meadow lands and for the fertilization of oats, carrots, beets, spinach, and cabbage was described by Raupp.[190] When the liquor was diluted with an equal volume of water and 2 liters of the mixture was applied per square meter of meadow land, the yield of dry hay was increased by 150 percent. By application of a mixture consisting of 1 liter of the liquor to 3 liters of water per square meter, yields of vegetables were increased from 150 to 300 percent. No unfavorable

[182] Bailey, T. L., *Gas J.*, **159**, 213–4 (1922).

[183] Mews, J., *Gas- u. Wasserfach*, **65**, 123–4 (1922); *Gas J.*, **157**, 700 (1922).

[184] Shnidman, L., *Proc. Am. Gas Assoc.*, **1932**, 950–69.

[185] Demolon, A., *Ann. sci. agron.*, [4] **1**, 178–214 (1913); *Chem. Abs.*, **7**, 2277 (1913).

[186] Russell, E. J., and Buddin, W., *J. Soc. Chem. Ind.*, **32**, 1136-42T (1913).

[187] Beaumont, A. B., and Larsinos, G. J., *Am. Fertilizer*, **76**, No. 9, 9, 10, 28, 30 (1932).

[188] Mach, F., *J. Ind. Eng. Chem.*, **11**, 156 (1919).

[189] Paturel, *J. usines gaz*, **53**, 11 (1929); *Génie civil*, **94**, 416 (1929).

[190] Raupp, K. H., *Gas- u. Wasserfach*, **73**, 230–3 (1930).

results due to action of the compounds in the liquor were noted.

Schuster [191] stated that poisonous sulfides and thiocyanates in the liquor are readily oxidized in well-aerated ground. Gas liquor should be applied several weeks before sowing. Because of the tarry constituents, top dressing should be avoided, except for cultivation of grasses. The use of gas liquors absorbed in peat is preferable to its direct use; this is true also for the waste liquor after distillation without lime.

Experiments carried out at the Mariendorf gasworks in Berlin on the admixture of 1 percent by volume of weak ammonia liquor with city sewage were described by Weldert and coworkers.[192] Most of the ammonia in the liquor was combined with carbon dioxide. No injury resulted from use of the mixture on sewage farms, the vegetables had no peculiar odor, and the taste of milk from cows pastured on grass or beets was unaffected. The amounts of substances retained on two test fields, each about 0.3 acre, one fed with the sewage and the other with the sewage-ammonia liquor mixture, are shown in Table XXV.

In later tests,[193] the proportion of ammonia liquor in the mixture was increased to 3 percent with satisfactory results. Putrefaction in the drainage water did not occur during addition of this proportion of liquor. A 3 percent admixture of liquor with sewage distributed over the surface proved harmful to the early growth of young grass, but by the fifth cutting the yield was about 10 percent greater than on a section fed only with sewage.

At Marienburg, pot tests were carried out to determine the effect of liquors containing 2 percent ammonia on oats and mustard plants. They indicated that good results could be obtained on the better or heavier soils, according to Bimschas.[194] Poor results were obtained on a poor, sandy soil, even though potash and phosphate were added.

Purification of the gas liquor to be used for fertilizer has also been patented.[195] Cyanide was converted to thiocyanate, sulfur was separated from sulfur compounds by treatment with air, and the liquor was distilled. The nonvolatile compounds were left in the retort.

The cost of transportation and distribution of ammoniacal liquor over the soil will usually be prohibitive. For a very small plant located near a large area of agricultural land, disposal of the liquor as a fertilizer might be more economical than recovery of ammonia in the still.

USES FOR CONCENTRATED AMMONIA LIQUOR

Pure concentrated ammonia liquors have been oxidized to nitric oxide without injury to platinum catalysts, but crude liquors containing sulfur rendered the gauze catalysts inactive unless the sulfur was removed.[196]

TABLE XXV

Results from Use of Ammoniacal Liquor on Sewage Farms [192]

| | Irrigated with | |
	Sewage	Sewage-Liquor Mixture
Kilograms ammonia nitrogen retained	165	376.4
Kilograms phenol retained	18.5	95.6
Kilograms organic matter retained (calculated from KMnO₄ demand)	1,842.0	856.3

[191] Schuster, F., *ibid.*, **74**, 318–9 (1931).

[192] Weldert, R., Kolkwitz, R., Ziehe, Nehm, Köhler, H., Bausch, H., and Langbein, *ibid.*, **74**, 1005–10, 1030–4 (1931).

[193] Weldert, R., Kolkwitz, R., Nehm, Köhler, H., and Bausch, H., *ibid.*, **75**, 926–30 (1932).

[194] Bimschas, *ibid.*, **74**, 13–6 (1931) ; *Gas J.*, **193**, 324 (1931).

[195] Gesellschaft für Landwirtschaftlichen Bedarf and Mandelbaum, I. R., Brit. Pat. 153,006 (1920).

[196] Perley, G. A., and White, W. P., *Ind. Eng. Chem.*, **21**, 564–7 (1929).

Pure liquid ammonia was prepared from ammoniacal liquor by Zaniboni.[197] The ammonia was scrubbed from the still gases by an absorbing solution which was then heated in a closed condensing system until the expelled ammonia liquefied. By using ammonium thiocyanate and ammonium nitrate solutions, practically 100 percent ammonia was produced.

Concentrated ammonia liquors have been suggested for the removal of hydrogen sulfide, carbon dioxide, and hydrogen cyanide together from coal gas.[198]

Methods for Disposal of Ammoniacal Liquor

The following methods for the disposal of ammoniacal liquors or wastes may be employed: (1) discharge into rivers, lakes, or the sea; (2) discharge into or on the ground; (3) evaporation or use in plant processes; or (4) treatment in sewage-disposal plants.

DISCHARGE INTO A STREAM

Discharge of waste liquors from the ammonia still into a stream, although usually the most convenient method of disposal, is open to serious objections, the most important of which is the possible effect on water supplies. The 1925[199] report of the Advisory Committee on Official Water Standards of the United States Treasury Department specified that "the water should be clear, colorless, odorless, and pleasant to taste, and should not contain an excessive amount of soluble mineral substances."

Discharge of still waste or other ammoniacal liquor into a stream may have one or more of the following effects:

1. Organic matter in the liquor produces odors and tastes in the water, particularly after chlorination.

2. The high oxygen-absorbing capacity of the liquor uses up the dissolved oxygen in the water. Two effects are then possible: (a) putrefactive decomposition of the organic matter in the water may give rise to foul-smelling compounds, such as hydrogen sulfide and mercaptans; (b) depletion of the oxygen in the water will cause the death by suffocation of higher forms of life, such as fish.

3. Inorganic salts in the liquor increase the hardness and the corrosive action of the water.

4. Dissolved compounds in the liquor exert a toxic effect on the flora and fauna of the water, including such life as bacteria, fish, and oyster beds.[200]

5. Insoluble matter, such as the carbonates, settles to the bottom and chokes out the life there.

The increasing public consciousness of the value of water supplies is rendering disposal of unpurified waste waters into public bodies of water increasingly difficult. Untreated still wastes have proved so objectionable that their discharge into lakes or streams has in many places been prohibited.

Taste and Odor Production. The most serious objection to the discharge of ammoniacal liquor into a stream is the development of medicinal tastes and odors in chlorinated water which contains the liquor.

The danger in distributing water containing a taste or an odor has been emphasized by Jordan.[199] "Unpleasant taste is the most serious quality affecting the goodwill of the community towards its drinking

[197] Zaniboni, R., U. S. Pat. 1,954,973 (1934); *Acqua e gas,* **23,** 47–57 (1934); *Chem. Abs.,* **29,** 6734 (1935).

[198] See Chapter 11 in ref. 11. See also pp. 261–70 in ref. 66.

[199] *U. S. Pub. Health Service, Pub. Health Repts.,* **40,** 693–722 (1925); Jordan, H. E., *Ind. Eng. Chem.,* **21,** 152–8 (1929).

[200] Willien, L. J., *Gas Record,* **18,** No. 8, 31–4 (1920); *Gas Age,* **46,** 349–52 (1920).

water. Boards of health may point out that the supply is not safe, but as long as it tastes well it is difficult to make the average citizen believe that it is not safe, and conversely, it is very difficult to make the average citizen believe that bad-tasting water is safe."

The medicinal tastes and odors are usually due to reactions of the phenols in the liquor with the chlorine which, in most water-treating plants, is added during the purification process. Chlorophenols are formed. The following equation shows one of the reactions which may occur:

$$C_6H_5OH + 3Cl_2 \rightarrow C_6H_2Cl_3OH + 3HCl$$
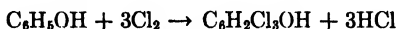
The medicinal tastes of chlorinated phenolic compounds are exceedingly penetrating and have been detected at extremely high dilutions in water. According to Bach,[201] chlorophenol is plainly tasted at concentrations of 1 part in 10 million. Theriault[202] found that chlorophenol tastes were faintly noticeable at concentrations of 1 part in a billion when the chlorine dosage was carefully adjusted, and unmistakable at 5 parts per billion. Kohman[203] detected a chlorophenol taste after chlorination of water containing 1 part of phenol in 750 million. It was essential that the chlorine be present in the proper concentration. A slight excess destroyed the taste. Chlorophenol compounds in water containing phenol, which had been subsequently chlorinated, not only imparted a very penetrating odor to the water but also was responsible for a medicinal taste which developed in canned food in which the water was used.

Dieterle[204] pointed out that the psychol-ogy of taste is very involved and that taste results are not absolute. In his tests carried out with a number of observers, the least amount of phenol which could be detected was 1 part in 75 million. Pittsburgh tap water was used, and the mixture chlorinated to 0.3 part per million. Brown,[205] at Milwaukee, found that water containing 1 part of phenol in 500 million, when treated with 0.3 part per million of chlorine, developed a taste which rendered it unsuitable for drinking or cooking purposes.

Not only phenols produce a medicinal taste in water on chlorination; according to Adams,[206] similar tastes will be produced by cresols, xylenols, salicyl derivatives and their isomerides, cresotinic acids, metals, especially zinc and lead, and iodides. Phenolic substances may originate from other sources than the waste liquors from carbonizing operations, such as washings from tarred roads, air-borne volatile phenolic substances, creosoted wood pipes, and tarred cord in pipe joints. Domestic sewage also contains phenols.

Difficulties from phenolic tastes and odors are described frequently in the literature. The situation in the Ohio River valley was at one time particularly aggravated, owing to the number of coke plants which discharged waste liquor from their ammonia stills into the river and its tributaries,[207] but the installation of dephenolizing plants has largely prevented further occurrence of

201 Bach, H., *Z. angew. Chem.*, **39,** 1093–8 (1926).

202 Theriault, E. J., *Ind. Eng. Chem.*, **21,** 343–6 (1929).

203 Kohman, E. F., *ibid.*, **15,** 518 (1923).

204 Dieterle, E. A., *Gas Age*, **46,** 427–8 (1920).

205 Brown, R. B., *Am. Gas Assoc. Monthly*, **1,** 189–90 (1919).

206 Adams, B. A., *Water & Water Eng.*, **33,** 109 (1931).

207 Leitch, R. D., *U. S. Pub. Health Service, Pub. Health Repts.*, **40,** 2021–6 (1925). Hodge, W. W., *W. Va. Univ. Coll. Eng., Tech. Bull.* **1,** 40–54 (1927) (Series 13, No. 3). Streeter, H. W., *U. S. Pub. Health Service, Pub. Health Repts.*, **44,** 2149–56 (1929). Waring, F. H., *Am. J. Pub. Health,* **19,** 758–70, 817–22, 929–34 (1929).

the taste troubles.[208] Sporadic appearance of phenols in the river under conditions of recovery are most likely to occur in the cold months of the year, because of several basic causes: [208] (1) biochemical processes for stream self-purification are retarded under conditions of low temperature; (2) surface drainage from stations where wastes are disposed of in quenching hot coke find their way to streams without purification by soil percolation, when the ground is covered with snow and ice; and (3) accidental leaks and spills constitute an important source of phenol contamination. In addition, phenol may be fixed in ice and liberated in quantity during thaws. Also, gas plants tend to operate a little faster during the winter, so that the volume of liquor is greater.[209]

Other locations [210] where troubles have occurred are in the vicinity of the coke plants of the Great Lakes region. These troubles also have been largely minimized by treatment of the waste, either by dephenolization, or in sewage-purification plants.[211] In the Ruhr region in Germany, phenol pollution of the rivers has been a problem. Wiegmann [212] has reported that dephenolization of all the liquors, followed by biological treatment and retention in storage ponds, is necessary for a satisfactory solution of problems of elimination of taste and odor of waste liquor before discharge into streams serving for public water supplies.

Oxygen Absorption of Ammoniacal Liquors. Organic matter in sewage or industrial wastes entering a stream is decomposed mainly by the oxidizing action of bacteria or other organisms which are found in the water. These reactions consume the oxygen dissolved in the water, sometimes to such an extent that the water cannot support aquatic life. In water denuded of its oxygen, other bacterial reactions may take place which result in the production of foul-smelling compounds and unpleasant conditions generally.

In the opinion of the British Royal Commission on Sewage Disposal,[213] domestic sewage can be discharged into water without previous purification, when the volume of the water is at least 500 times the volume of the sewage. At this dilution, the oxidation which occurs subsequent to the discharge does not unduly deplete the dissolved oxygen content of the mixture, and little damage or nuisance is caused.

Trade wastes may have a much higher oxygen absorption than domestic sewage, and such wastes will require a proportionally greater dilution. It is now seldom possible for a plant to discharge its waste liquor into a stream, unless dilution adequate to prevent the formation of objectionable tastes and odors or of toxic concentration is possible. Sometimes, even though the degree of ultimate dilution is satisfactory, the rate of diffusion is so slow that local toxic concentrations persist for a long time and give rise to trouble. In such circumstances, preliminary mixing of the waste, with other sewage for instance, facilitates further dilution in the stream into which the mixture flows.

208 Hatch, B. F., *Blast Furnace & Steel Plant*, **18**, 618–19, 621 (1930).

209 Shaw, J. A., private communication, 1941.

210 Emerson, C. A., Jr., *Trans. Am. Soc. Civil Eng.*, **85**, 484–5, 506–8 (1922); *Eng. Contr.*, **57**, 132–3 (1922).

211 Ellms, J. W., *Eng. News-Record*, **92**, 453 (1924). Bundesen, H. N., *Water Works*, **67**, 240–6 (1928). Waring, F. H., *Am. J. Pub. Health*, **19**, 758–70, 817–22, 929–34 (1929). Hatch, B. F., *Blast Furnace & Steel Plant*, **17**, 1493–6, 1797–1800 (1929), **18**, 296–8, 618–9, 621 (1930).

212 Wiegmann, H., *Gas- u. Wasserfach*, **75**, 433–6 (1932).

213 Royal Commission on Sewage Disposal, *8th Report*. See also p. 24 of ref. 11.

The oxygen requirements for the decomposition of the organic matter in ammoniacal liquor or other organic waste can be measured by two methods: (1) the oxygen-consumed test; and (2) the biological oxygen demand, or B.O.D.

The oxygen-consumed test determines the amount of potassium permanganate destroyed in oxidizing the organic matter in a solution acidified with sulfuric acid under standardized conditions.[214] Organic compounds are not oxidized by potassium permanganate with equal facility,[215] so that in the test only a portion of the organic matter is destroyed. The proportion varies in different samples and, in particular, with different kinds of wastes. Although under the test conditions the organic matter may not be completely oxidized, the relations between the proportion oxidized and the total amount present in ammoniacal liquor and in domestic sewage, respectively, are fairly constant. In these fluids the test can be used to measure the relative amounts of oxidizable organic matter present.[216] A further discussion will be found in the methods of analysis.

The biological oxygen demand test aims to determine the amount of oxygen required for the biochemical decomposition of sewage or other wastes, and the rate of its consumption, by producing biochemical conditions of oxidation. The sewage is diluted with a known amount of aerated pure water of known oxygen content, and the oxygen consumed during the incubation of the diluted sewage for a definite time at a definite temperature is determined.[217] This test is much to be preferred for liquors undergoing biological oxidation, but it suffers from the disadvantage that the results are not known for 5 days.[216]

Effects of Ammoniacal Liquors on Fish and Other Forms of Life. Many of the compounds dissolved in ammoniacal liquor have proved toxic to fish when present in sufficiently high concentrations. Susceptibility of the fish has varied with such factors as kind and size of fish, length of exposure, temperature and dissolved oxygen concentration of the water, and the time of the year.

Toxic concentrations for a number of coal-tar compounds to five kinds of fish, when exposed for 1 hour, were determined by Butterfield[218] at different times of the year (see Table XXVI). In the right-hand column of the table are included concentrations, which Shelford[219] found would kill American orange-spotted sunfish in 1 hour.

Butterfield[218] found that observations on goldfish were similar to those on carp, with which they are closely allied, but were useless as an indication of results on perch and trout, which thrive only in well-oxygenated waters. Perch, dace, and gudgeon were satisfactory alternatives to trout. Minnows were even more sensitive to most poisons.

Shelford's[219] work showed that smaller fish were more readily affected than the larger, and that the most sensitive of all were probably the smallest fry. Of the 34 representatives of the chief groups of compounds found in gas liquor and gas, which were studied by Shelford, 31 were fatal in concentrations between 1 and 1,500 parts

214 *Gas Chemists' Handbook,* Am. Gas Assoc., New York, 1929. Bailey, T. L., *Ann. Rept. Alkali, &c., Works,* **64,** 21–2, 24–5 (1928). See also pp. 185–6 of ref. 11.

215 Ivekovic, H., *Plyn, Voda, zdrav. Tech.,* **17,** 408–412 (1937); *Chem. Zentr.,* **109,** I, 143 (1938).

216 Chapter 4 of ref. 11.

217 Am. Pub. Health Assoc., *Standard Methods of Water Analysis,* 8th ed., Lancaster Press, Lancaster, Pa., 1936, Pt. III, Sect. XII.

218 Butterfield, W. J. A., *J. Soc. Chem. Ind.,* **47,** 293–311T (1928).

219 Shelford, V. E., *Bull. Illinois State Lab. Nat. History,* **11,** 381–412 (1917); **13,** Art. 2 (September, 1918).

TABLE XXVI

RELATIVE TOXICITY TO FISH OF AQUEOUS SOLUTIONS OF COAL-TAR COMPOUNDS [218, 219]

Fish	Carp	Gudgeon	Dace	Perch	Trout	American Sun
Size or age	8 in.	5–8 in.	8–10 in.	1–2 yr	1–2 yr	0.14–0.21 oz
Compound	Concentration in parts per million which will kill fish in 1 hour. (Month of observation in parentheses)					
Ammonia	50 (N, D)	35 (S)	30 (O)	18 (F, D)	18 (S, D)	7.5
		30 (N)	25 (N)	25 (S)		
Ammonium sulfate		1,000 (S)	1,000 (O)	600 (Jn)		46
Ammonium thiocyanate		500 (S)	600 (O)	450 (Jn)		29
Phenol	400 (D)	100 (O, D)	100 (N)	50 (Mr)	30 (My)	72.5
				30 (My)	25 (S)	
				25 (S)	50 (D)	
	Mixed			100 (D)		
o- and m-cresol	250 (O)	110 (O, D)	110 (D)	80 (D)	10 (Au)	60 (o- only)
Naphthalene	Not toxic (S)	Not toxic (S)	Not toxic (O)	Suspended solid (Ja)	Suspended solid 45 min (Ja)	4.5
Pyridine		Not toxic (D)	Not toxic (D)		2,000 (Jn)	1,530

(Suspended solid of naphthalene refers to vigorous shaking of powdered naphthalene with water and rapid filtration.)

per million in 1 hour. The fish usually reacted positively to the mixtures studied; i.e., they entered polluted water from pure water readily, and turned back into polluted water on encountering pure. This increased the danger to the fish.

The toxic limit of a compound to fish has been defined by the South Metropolitan Gas Company [220] as the concentration in water which just caused the fish to turn on their backs in 60 minutes' exposure. This limit is definitely lower than the killing limit. Toxic limits for several compounds were determined on trout, Table XXVII.

TABLE XXVII

TOXIC LIMITS OF FOUR COAL-TAR COMPOUNDS ON TROUT [220]

Compound	Toxic Limit parts per million	Month
Phenol	10–12.5	January, February
	7.5	July
p-Cresol	7.5	February, July
Pyridine	400	April
Naphthalene	3.75	November

[220] South Metropolitan Gas Company, J. Soc. Chem. Ind., 56, 184-90T (1937).

The toxicity of phenol is lowered if the water is aerated, as shown by Eldridge.[221] Over 20 parts per million killed fish in an aerated sample of water, but in unaerated water, 10 to 20 parts per million were fatal. The toxicity of cresol was the same, 15 to 20 parts per million, in both aerated and unaerated water.

Hubault [222] investigated the toxicity of organic compounds which may be present in waste waters from carbonizing operations, high as well as low temperature, on roach. The toxicities of phenols at different temperatures, and of several other hydrocarbons, are given in Table XXVIII.

Demyanenko [223] found that water is injurious to fish if the alkalinity is more than 8 cubic centimeters or the acidity more than 1.6 cubic centimeters of normal solution per liter. The following data on the

[221] Eldridge, E. F., Bull. Mich. Eng. Expt. Sta., 60, 49 (1934).

[222] Hubault, E., Compt. rend. acad. agri. France, 21, 228, 255, 714 (1935), 22, 130, 324 (1936).

[223] Demyanenko, V., Hig. i. Epidem. (U.S. S.R.), 10, No. 6/7, 13 (1931); Chem. Abs., 27, 2746 (1933).

TABLE XXVIII

TOXICITY OF ORGANIC COMPOUNDS IN WASTE LIQUORS ON ROACH [222]

Phenol	30 ppm in 2.5 hr at	9.5° C
	20	4.5	9.5°
	20	1.83	21°
o-Cresol	110	5	9.5°
	70	3	21°
n-Pentane	>60	1–4	20.2°
n-Heptane	30	1–4	21.1°
Benzene	20	1–4	9 and 16.3°
Toluene	>9	1–4	6.8°
Toluene	3	1–4	20°
Thiophene unaffected in 1.8		4	11.7°

toxicity of specific compounds were reported: naphthalene, lethal at 10 parts per million; calcium chloride, injurious at 12,-500 parts per million; ammonium thiocyanate, deadly at 200 parts per million; and pyridine, feeble effect at 1,000 parts per million. Fish were able to live for long periods in water containing 15 parts per million of phenol, but the flesh acquired a phenolic odor.

Härdtl [224] reported that phenol was toxic to perch at concentrations of 5 parts per million. Helfer,[225] on the other hand, stated that 0.1 part per million of phenol was harmful. From his work on the bacterial oxidation of phenol in water, Müller [226] suggested that damage to fish in streams might be caused by lack of oxygen, due to the biochemical oxidation of concentrations of phenol considerably below those which would cause direct damage to the fish. In laboratory experiments, Kalabina [227] found that fish could tolerate phenol concentrations of 4 to 15 parts per million, but they were found in water only when the concentration was not greater

than 0.2 part per million. He pointed out that the effect of a waste containing phenol did not necessarily depend on the phenol alone but also on other compounds, such as naphthalene, cyanides, and resins.

Attention should be called to the work of the Water Pollution Research Board on the pollution from coke-oven wastes in the estuary of the River Tees in Great Britain, during 1930 and 1931. The results have been described by Southgate and his colleagues.[228] Salmon and sea-trout fisheries had become almost worthless, because the polluted water killed the young fish, or smolts, on their spring migration from the spawning grounds in the upper reaches of the river to the sea. The pollution was finally traced to cyanide in final cooler water from coke plants. Examination of dying trout showed a brightening of the gill color and a highly oxygenated condition of the blood, both characteristics of cyanide poisoning. Tests on trout showed that they were rendered helpless by immersion for less than an hour in a solution of potassium cyanide equivalent to 0.14 part per million of cyanide at 5° C. The toxicity of cyanides was greatly increased by an oxygen deficiency in the polluted water. Removal of cyanide from the polluted water eliminated the toxicity. The toxic effect of cyanide upon shrimp varied greatly with the species.

The degrees of toxicity of such tar derivatives as benzene and naphthalene and of cyanides and thiocyanates to *Daphnia*

224 Härdtl, H., *Z. Fisch.*, **32**, 459 (1934); *Wasser u. Abwasser*, **33**, 223 (1935).

225 Helfer, H., *Kleine Mitt. Ver. Mitglied. Ver. Wasser-, Boden-, u. Lufthyg.*, **12**, 32 (1936).

226 Müller, A., *Tech. Gemeindeblatt*, **35**, 148 (1932).

227 Kalabina, M. M., *Z. Fisch.*, **33**, 295 (1935).

228 Robertson, R., and Calvert, H. T., *Dept. Sci. Ind. Research (Brit.) Rept. for the Year Ended 1931*, 37 pp.; *ibid.*, *1933*, 56 pp.; *Tech. Paper* 5 (1935), 171 pp. Southgate, B. A., et al., *J. Marine Biol. Assoc. United Kingdom*, **18**, 671–6 (1933), **20**, 717–24 (1936); *Gas J.*, **202**, 216–8 (1933); *Gas World*, **98**, No. 2544, Coking Sect. 56–9 (1933); *Biochem. J.*, **26**, 273 (1932), **27**, 983 (1933); *Yearbook, Coke Oven Managers' Assoc.*, *1934*, 203–13. Tupholme, C. H. S., *Ind. Eng. Chem.*, *News Ed.*, **11**, 211 (1933).

were determined by Kazachkov.[229] In mixtures of these substances the toxic effect was additive.

A very good still waste, according to Ott,[230] has been shown to poison fish up to a dilution of 1 to 200. Hodge and Herndon [231] found that the dephenolized still wastes from two American plants did not injure fish life on dilution 1 part to 100 with river water. A review of the harmful effect of ammoniacal liquors on fish was made by Brender à Brandis and Keeman.[232]

In order to determine the physiological action of phenol-contaminated waters, rats were given only phenol solutions to drink by Heller and Pursell.[233] In concentrations up to 0.1 per cent, no unfavorable action was noted.

Disappearance of Phenol in Water. Phenol in natural water slowly disappears. The decrease in the phenol content has been noted by a number of investigators. As a result of experiments on goldfish in water containing small amounts of phenol, Bach [234] reported that, in the absence of sludge deposits, still or slowly moving water has a greater self-purifying power than swiftly flowing water. When present in a concentration of 10 parts per million, the phenol disappeared at the rate of 0.7 part per million per day.

Müller [235] showed that the disappearance of phenol from water depended on bacterial action in the presence of oxygen. Phenol in a sterile solution was not decomposed. In water covered with a layer of paraffin, phenol disappeared until the oxygen in the water was exhausted, when the reaction ceased. The use of phenol as a foodstuff by the bacteria was shown by the increase in the bacterial count during decomposition of the phenol in water. The addition of nutrient material to the water increased bacterial development but slowed down phenol decomposition, thus indicating that, as long as a more easily utilizable source of carbon was at their disposal, the bacteria did not attack the phenol.

Mischonsniky [236] found that 10 parts per million of phenol in the water of an aquarium containing soil and plants as well as fish was decomposed at the rate of 3 to 5 parts per million per 24 hours with a reduction in the oxygen content of the water. He concluded that small quantities of phenol facilitate chemical reactions which give rise to a positive catalysis, and thus accelerate the decomposition and oxidation of organic matter.

In a study of the appearance of chlorophenol tastes and odors in water supplies of the Ohio River cities, Streeter [237] showed that the concentration of the phenolic tastes tended to become reduced in passing downstream to a greater extent than could be accounted for by dilution or by any other wholly physical influence. The times when phenol pollution reached points far downstream coincided with shortened times of flow and relatively low stream temperatures, both of which conditions tend to reduce the natural purification effects in streams. Streeter advanced the theory

229 Kazachkov, L. I., *Hyg. serv. sanit.*, **2**, No. 9 -10, 18 (1937) ; *Bull. off. int. hyg. publ.*, **30**, 1875 (1938) ; *Chem. Abs.*, **33**, 4359 (1939).

230 Ott, E., *Gas- u. Wasserfach*, **67**, 140–1 (1924).

231 Hodge, W. W., and Herndon, L. K., *West Va. Univ. Eng. Expt. Sta., Tech. Bull.* **5**, 48–61 (1932) ; *J. Am. Water Works Assoc.*, **25**, 1827 (1933).

232 Brender à Brandis, G. A., and Keeman, W., *Het Gas*, **54**, 2–13 (1934).

233 Heller, V. A., and Pursell, L., *J. Pharmacol.*, **63**, 99–107 (1938).

234 Bach, H., *Gesundh.-Ing.*, **52**, 796 (1929).

235 Müller, A., *Tech. Gemeindeblatt*, **35**, 148 (1932).

236 Mischonsniky, S., *14me. Congr. chim. ind., Paris*, October, 1934, 11 pp. *Chimie & industrie*, **32**, 89 (1934).

237 Streeter, H. W., *Am. J. Pub. Health*, **19**, 929–84 (1929).

that a natural process of biochemical oxidation takes place in the stream. The lesson derived from this theory was that the important sources of frequent phenol pollution of a water supply were likely to be found in the near vicinity, though occasional pollution may have a more distant source.

An investigation made by Kalabina and Rogowskaya [238] on phenol in pure solutions and in gasworks waste waters showed that the decomposition was a biochemical reaction, which was dependent on the temperature, aeration, the development of bacteria and other aerobic micro-organisms, and the presence of nitrogenous and mineral nutritive material for these micro-organisms. Phenol decomposed more rapidly in pure solutions than in gasworks waste liquors. In solutions containing up to 2 grams per liter, the phenol might serve as a source of carbon for certain bacteria. In open jars, the rate of decomposition of phenol was occasionally as high as 100 parts per million per liter per day and averaged 57 parts per million per liter per day.

Addition of 10 percent of sewage to water containing phenol increased the rate of decomposition of the phenol but did not affect the final result. [239] In running water, the rate of decomposition of phenol increased with the rate of flow. In experiments on the disappearance of phenol in the Kalmius and Gruskaja Rivers, it was found that traces of phenol decomposed very slowly and remained in water much longer than larger amounts.

The investigations of the River Water Investigation Board at Magdeburg confirmed the biological oxidation of phenol in river water. [240] The decomposition proceeded more rapidly in warm than in cold weather and was delayed when large quantities of phenol (about 130 parts per million) were present.

The conclusion that the disappearance of phenol in streams is due to a biochemical action is supported by the work of the investigators quoted. The apparent contradictions in some of their results would possibly be reconciled were the phenol concentration, strain of bacteria, degree of aeration, and the like, the same.

DISCHARGE OF LIQUORS INTO THE GROUND

Disposal of ammoniacal liquors or wastes by discharge into the ground is seldom possible except in very small carbonizing operations. Discharge into an opening, such as a disused well, is dangerous, because the ultimate fate of the liquor is unknown. It may be gradually dissipated and purified as it seeps through the soil. On the other hand, it may find its way into some water-bearing strata or percolate unchanged through the layers of soil to drain into a stream. In such a case, the pollution would probably not appear immediately, but when it did, deposits of the material in the contaminated soil would cause the trouble to persist over a period of time. [241] The disposal of phenolic waste liquor at Buffalo, N. Y., by pumping into drilled wells which penetrated a salt stratum has been reported by Devendorf. [242]

Disposal of ammoniacal liquor by sprinkling over the surface of land is less open to the danger of contaminating water. When sprinkled on land, the ammoniacal liquor, instead of the limed still waste, is used, so that advantage can be taken of

238 Kalabina, M. M., and Rogowskaya, C., *Z. Fisch.*, **32**, 153–70 (1934) ; *Chem.-Ztg.*, **58**, 38 (1934) ; *Wasser u. Abwasser*, **32**, 124–5 (1934) ; *Chem. Abs.*, **28**, 4208 (1934).

239 Kalabina, M. M., *Z. Fisch.*, **33**, 295 (1935).

240 Nolte, E., *Deut. Landeskultur-Ztg.*, **7**, 14 (1938) ; *Chem. Abs.*, **33**, 4717 (1939).

241 Chapter 7 of ref. 11.

242 Devendorf, A., *Contract Record & Eng. Rev.*, **44**, 500 (1930).

the fertilizing action of the ammonia. The liquor is diluted by the moisture in the soil, and the loss of ammonia by evaporation is relatively small. Biological oxidation usually sets in and rapidly destroys the organic matter, including the tar acids. The discharge of final cooler water of a Belgian coking operation onto made-up ground has been described.[243] Analyses showed that the water had been thoroughly purified by the time it reached the Meuse River.

Sen-Gupta [244] found that phenols and cresols were rapidly attacked in soils. The disappearance was probably brought about by several agencies, of which one, probably chemical or physicochemical, acted instantaneously. A slower decomposition was largely brought about by micro-organisms. The evidence tended to support the hypothesis that the various types of phenol destruction were due fundamentally to one agent, manganese dioxide.

The effect of the liquor on plant life is discussed under use of ammoniacal liquor as a fertilizer.

EVAPORATION OF LIQUORS

If the liquor cannot be regularly discharged into a body of water, even after purification, it must ultimately be evaporated. The requirements for a successful evaporation process are three: [241] (1) a cheap source of heat must be available; (2) the gases produced must not pollute the atmosphere or attack the plant apparatus; and (3) the residue must be in a form which can easily be disposed of.

The following methods for evaporation have been used or suggested: (1) use of the liquor for quenching the incandescent coke from the ovens or retorts; (2) production of water gas in producers or water-gas sets;

and (3) evaporation by chimney gases. When liquor is evaporated, the salts are recovered, either in the solid form, or as a concentrated solution. The solids from still waste ordinarily are of no value and must be discarded in some way.

Coke Quenching. Use of ammonia still waste for quenching incandescent coke from the ovens is the most common method for evaporation. Gluud and Jacobson [245] indicated that, in quenching a ton of coke, 110 to 120 gallons of water would be evaporated, equivalent to 80–90 gallons of water per ton of coal charged. This volume is much greater than the volume of still waste produced in a semi-direct sulfate plant and represents a large proportion of the waste ordinarily produced in an indirect-type plant.

The objections which have been raised to use of waste liquor for coke quenching are as follows: (1) the quality of the coke is affected; (2) the rate of corrosion of plant steel work is increased; and (3) the quenching fumes contaminate the atmosphere and adjacent ground.

The experience at Clairton, the largest coke plant in the world, was described by Marquard.[246] In quenching, approximately 400 gallons of water per ton of coal was sprayed onto the incandescent coke, of which approximately 20 percent was evaporated. The loss of water was replaced by the addition of several phenol-bearing plant wastes, including the waste from the ammonia stills. The calcium chloride from the waste liquor built up in the quenching water to about 2.5 percent. A considerable amount of this concentrated liquor became mechanically entrained in the current of steam and was distributed as a spray over

243 Anon., *Colliery Guardian,* 141, 1125 (1930).
244 Sen-Gupta, N. N., *J. Agric. Sci.,* 11, 136–58 (1921), 15, 497–515 (1925).

245 See p. 403 of ref. 2.
246 Marquard, F. F., *Am. J. Pub. Health,* 18, 1497–1500 (1928). Bundesen, H. N., *Water Works,* 67, 240–6 (1928).

a wide area. All steel work about the plant was subjected to an abnormal rusting action from this entrained calcium chloride or from the hydrochloric acid produced by contact with the incandescent coke. Large settling basins for the separation of coke dust from the waste liquor from the coke quenching, and a mixing tank for adding make-up water, were required. Redesign of quenching water pumps to reduce abrasion was necessary. Coke produced by liquor quenching has a pronounced odor which interferes with its use as a domestic fuel. The moisture content is increased by reason of the calcium chloride concentration. In addition, the lime may discolor the coke.

Waring[247] stated that the life of coke-plant steel work, variously estimated at 7 to 10 years when using clean water for quenching, was cut to 2 to 4 years when using phenolic wastes.

Prüss[248] found that the phenol carried off from the quenching tower in the spray and steam was deposited on neighboring ground, which it damaged, and from which it reached the rivers. In addition to imparting a phenolic odor to the coke, use of the still waste destroyed the color. In a case cited by Tibbetts,[249] use of the strongest portion of the gas liquor for coke quenching did not stop pollution, and a plant for concentration of the liquor was erected.

Tests were made by Marson and Briscoe[250] on the use of diluted ammoniacal liquor for quenching metallurgical coke.

Neither the appearance, shatter test, combustibility, nor sulfur content of the coke was affected, and the authors concluded that harm to coke for metallurgical, domestic, or water gas use by this treatment was unlikely. The experience of coke-oven operators with ammoniacal liquor, as reported to the authors, indicated that the odors produced on quenching were no worse than when water was used, since the ammonia and hydrogen sulfide appeared to have been destroyed on the hot coke. About 330 gallons of liquor per ton of coke was used for quenching, of which about 155 gallons was evaporated. Analyses of the ammoniacal liquor, quenching liquor, and drainings from the quenching car will be found in Table XXIX.

With up to 10 percent still waste in the quenching water, Kapper[251] stated that the appearance of the coke was not harmed but that unpleasant odors might develop in storage. Coke used for water filters must be quenched with fresh water alone. He considered the use of undiluted waste liquor for quenching dangerous to workers.

In order to avoid tar acid odors on coke, Sperr[252] recommended the use of still waste for a preliminary quenching, followed by use of fresh water. Still[253] proposed a three-stage quenching, fresh water, followed by still waste, and, finally, fresh water. The following proportions were suggested per ton of coal: first quench, 24 gallons of fresh water; second, 36 gallons of waste; and, finally, 36 gallons of fresh water. About 75 gallons from waste and water would be evaporated.

247 Waring, F. H., *Am. J. Pub. Health,* **19,** 758–70, 817–22, 929–34 (1929).

248 Prüss, M., *Kleine Mitt. Mitglied. Ver. Wasser-, Boden-, u. Lufthyg.,* **5,** 278 (1929).

249 Tibbetts, C., *Dept. Sci. Ind. Research (Brit.) Water Pollution Research, Summary Current Lit.,* **9,** 40 (1936).

250 Marson, C. B., and Briscoe, H. V. A., *Gas World,* **94,** No. 2439, Coking Sect., 55–7 (1931); *Fuel,* **11,** 152–3 (1932).

251 Kapper, *Zentr. Gewerbehyg. Unfallverhüt.,* **23,** 160 (1936); *Dept. Sci. Ind. Research (Brit.), Water Pollution Research, Summary Current Lit.,* **9,** 427 (1936).

252 Sperr, F. W., Jr., U. S. Pat. 1,973,913 (1934).

253 Still, C., G.m.b.H., Ger. Pat. 629,369 (1936).

TABLE XXIX

ANALYSES OF AMMONIACAL LIQUOR AND QUENCHING WATERS [250]

	Ammonia Liquor from Scrubbers grams per liter	Diluted Liquor for Quenching grams per liter	Drainings from Quenching Car grams per liter
Free ammonia	19.1	3.64	1.19
Fixed ammonia	2.1	0.92	1.16
Total ammonia	21.2	4.56	2.35
Sulfate as H_2SO_4	0.27	0.48	0.61
Sulfide as H_2S	3.94	0.36	0.01
Thiocyanate as HCNS	0.94	0.52	0.51
Sulfite as H_2SO_3	0.12	0.05	0.03
Thiosulfate as $H_2S_2O_3$	1.0	0.72	0.73
Total sulfur as S	4.88	1.12	0.87
Cyanides as HCN	0.60	0.07	0.08
Chloride as HCl	2.32	1.21	1.41
Phenols as C_6H_5OH	0.82	0.27	0.18
Carbon dioxide	12.22	2.68	0.83
Total iron as Fe_2O_3	0.02	0.03	0.03
	parts per million	parts per million	parts per million
Oxygen absorption	7,460	1,750	1,180

Evaporation in Producers or Water-Gas Sets. Ammoniacal liquor has been evaporated in producers by using it to replace the water for cooling the grates or by spraying it into the producer for production of water gas.

In one plant,[254] spent liquor was distributed over the bars of a step grate producer, its rate of addition being regulated so that the ash pan remained just dry. Working in this way, it was found that 16 gallons of liquor per ton of coal carbonized in the retorts was evaporated in the producer. No unpleasant smell developed in the retort house, and no corrosion occurred in the producer, but a certain amount of attention was required. With more trouble, the ammoniacal liquor could be treated in the same way. Disposal of larger quantities in the producers would prove expensive and might interfere with normal operation.

A number of patents cover the use of ammoniacal liquors or wastes for the production of water gas, including those of Steere and Breisig.[255] The liquor was evaporated and the vapors introduced into the generator of the set.

Other investigators [256] have described the disposal of vapors from the ammonia still by passing them through a bed of glowing coke. A gas high in hydrogen but practically free from ammonia was produced.

Evaporation of Liquor by Flue Gases. Several processes for the concentration or evaporation of ammoniacal liquor or still waste by flue gases have been proposed. When the liquor is so evaporated, the vola-

254 Cobb, J. W., and Key, A., *Gas J.*, 196, No. 3571 Suppl., 14–6 (1931); *Gas World*, 95, 422–4, 466–9, 497 (1931). Botley, C. F., et al., *Trans. Inst. Gas Engrs.*, 80, 201–23 (1930); *Gas World*, 93, 594 (1930); *Gas J.*, 192, 730–3 (1930); *Inst. Gas Engrs., Commun.* 21, 12–30 (1930).

255 Steere, F. W., U. S. Pat. 1,752,037 (1930). Breisig, A., Austrian Pat. 128,024 (1931); Fr. Pat. 702,017 (1930).

256 Schuster, F., *Gas- u. Wasserfach*, 74, 318–9 (1931). Stief, F., *ibid.*, 80, 467 (1937); Ger. Pat. 641,267 (1987). Hamburger Gaswerke G.m.b.H., Ger. Pat. 641,267 (1937). Thau, A., *Gas Times*, 14, No. 171, 30–3 (1938).

tile compounds are carried off by the gases. In still waste, the amount of volatile matter will be negligible, but when ammoniacal liquor is evaporated, free ammonia and acidic gases will be vaporized. Key[257] indicated, however, that free ammonia and hydrogen sulfide react with the sulfur dioxide in the flue gases to produce solid substances.

The amount of liquor which can be evaporated will depend on the following factors:

1. The temperature of the flue gases. Gases from a waste heat boiler will be at a comparatively low temperature.

2. The dew point of the gas from the top of the stack. The gases must not be cooled below this temperature; otherwise the condensate formed may attack the steel or brickwork from which the stack is built.

3. The stack draft. The flue gases must not be cooled too low to give the required pull, or else a fan must be provided.

Introduction of the liquor as a spray into the base of the stack is not recommended, because there is danger that the liquor will attack the brickwork and deposits of solid salts will be difficult to remove.[257]

Cooper[258] patented an evaporator consisting of a series of trays, so fitted into the base of the chimney that their removal for cleaning was not difficult. The trays had ample surface to extract heat from the gases without greatly impeding their flow.

Whitcher[259] described an apparatus which consisted of a series of stepped, inclined planes located in horizontal flues.

The chimney gases swept through the flues against the flow of liquor, which was sprayed onto the uppermost planes.

Evaporation of Liquors in Boilers. Evaporation of ammoniacal liquors in boilers has been suggested. According to Bailey,[260] the accumulation of tar and dissolved compounds in the liquors necessitated blowing-down the boilers more frequently. Volatile impurities in the steam might also lead to corrosion of brass and other fittings.

Ammoniacal liquor was passed down a stripping column, in which the ammonia and more volatile compounds were distilled off with steam, according to patents of W. C. Holmes and Company.[261] The liquor was collected and evaporated in a boiler. Part of the steam produced by evaporation was used in the stripping column. The balance was available for steaming producers or retorts.

Special Methods for Evaporation of Liquor. Ammoniacal liquors have been evaporated in specially constructed evaporators. In one plant, the preheated liquor was regulated to fall in drops onto a steam-heated cylinder.[262] The resulting concentrated liquor was mixed with fuel and burned. The vapors were conducted into the boiler flues.

Marquard[263] passed ammoniacal liquor down a baffle tower against an upward current of hot gas. The liquor was recirculated until concentrated to the desired strength.

257 See pp. 60–1 of ref. 11.
258 Cooper, C., Henshaw, D. M., and W. C. Holmes & Co., Brit. Pat. 384,388 (1933).
259 Haywards Heath District Gas Co. and Whitcher, A. E., Brit. Pats. 407,374 (1934), 430,630 (1935).

260 Bailey, T. L., *Gas J.*, **159**, 213–4 (1922).
261 W. C. Holmes and Co., Cooper, C., and Henshaw, D. M., Brit. Pats. 392,553, 392,560 (1933), 407,801 (1934).
262 *Report on Purification and Disposal of Gas Liquors (West Riding of Yorkshire Rivers Board) (1936).* See also Chapter 7 of ref. 11.
263 Marquard, F. F., U. S. Pat. 1,455,299 (1923). Marquard, F. F., and Littler, C. W., U. S. Pat. 1,491,486 (1924).

The action of bacteria has been utilized to break down the organic compounds in ammoniacal liquors or still wastes to simpler substances which can be disposed of by discharge into streams with less difficulty. In several cities of the United States, liquors from coking operations and gas plants have been combined with ordinary domestic sewage and purified in sewage-disposal works. Purification with sewage has become the most common method for eliminating gasworks wastes in Great Britain, and bacterial purification processes have been employed in other parts of Europe.

Bacteria may be classified roughly into two types, aerobic and anaerobic, depending on whether oxygen is or is not necessary for their life and action. Domestic sewage contains in itself the necessary bacteria for its purification; and sewage purification, whether by land filtration, contact beds, sprinkling filters, or activated-sludge processes, is mainly the outcome of the activities of the bacteria, especially the aerobic class, on the organic matter present. Bacterial oxidation takes an appreciable time, and any increase in the concentration of the oxidizable organic matter tends to decrease the throughput of the plant.

Effect of Ammoniacal Liquors on Sewage. The high oxygen requirements of ammoniacal liquors and waste liquors are therefore important factors in the treatment of such liquors by biological processes. The B.O.D. and the oxygen-consumed tests for assessing these requirements have already been described.

Mohlman [264] published analyses which showed the effects produced on the characteristic properties of Chicago sewage by addition of small percentages of still waste. To a settled sewage of average strength,

[264] Mohlman, F. W., *Am. J. Pub. Health*, **19**, 145–56 (1929).

TABLE XXX

ANALYSIS OF SEWAGE PLUS AMMONIA STILL WASTE [264]

| | Raw Sewage | Sewage plus Waste Liquor | | | | Waste Liquor |
		0.5%	1%	2%	3%	
Nitrogen, total, ppm	18.6	19.4	21.0	23.4	25.8	
organic, ppm	3.4	4.2	5.6	7.8	9.8	
as NH$_3$, ppm	15.2	15.2	15.4	15.6	16.0	
B.O.D., 5-day, ppm	110	136	165	200	247	
10-day, ppm	120	170	210	225	310+	
Suspended solids, ppm						
total, ppm	74	82	87	108	136	
volatile, ppm	58	64	54	72	108	
fixed, ppm	16	18	33	36	28	
Oxygen consumed						
(KMnO$_4$ test), ppm	25.0	58.8	125.0	181.0	234.0	
Alkalinity as						
CaCO$_3$, ppm	320	322	324	328	332	
Phenol (calculated), ppm	0.02	14.5	28.9	57.8	86.7	2,886
Total solids, ppm	1,134	1,152	1,196	1,222	1,290	
pH	7.4	7.5	7.5	7.5	7.6	
Bacteria count, agar, 48 hr	343,000	380,000	880,000	880,000	289,000	

containing no industrial wastes, was added a typical still waste from a high-temperature coking operation, Table XXX.

Analyses of similar wastes have been reported by Key.[265] In Table XXXI are

TABLE XXXI

COMPOSITION OF SEWAGE AND SEWAGE PLUS STILL WASTE [265]

	Sewage	Sewage +0.4 Percent Limed Still Waste
	parts per million	
Ammoniacal nitrogen	30	30
Albuminoid nitrogen	10	10
Suspended solids	350	350
Chlorides, as HCl	150	171
Alkalinity as CaCO$_3$	500	510
Oxygen consumed, KMnO$_4$ test	100	138
dichromate test	300	325
Biological oxygen demand	500	520
Phenols	...	10
Thiosulfate	...	3
Thiocyanate	...	5

shown analyses of a representative sewage, before and after the addition of 0.4 percent of the limed still waste from a vertical retort plant.

The deleterious effect exerted on the oxygen-consumed value of the sewage by the addition of gas-plant liquors may be calculated approximately if the oxygen-consumed values for the sewage and the liquor, respectively, are known. By such calculations, Parker [266] has shown the effects of adding small proportions of two still wastes to a typical sewage, one the waste from horizontal retorts with an assumed oxygen consumption of 4,000, the other waste from continuous verticals with an assumed oxygen consumption of 7,500, Table XXXII.

The tables show that by the addition of 1 or 2 percent of gas liquor to domestic sewage the oxygen consumption may be increased by several hundred percent. In view of this important increase in the oxy-

gen consumption, it is not surprising that an ammoniacal liquor has often been regarded as a very objectionable constituent of sewage.

The oxygen-consumed test, however, cannot be relied on for assessing the effect of additions of such liquors on sewage. Potassium permanganate attacks only a small proportion of the oxidizable matter in sewage, whereas it oxidizes the greater portion of that in gas-plant liquors.[265]

Although the biological oxygen demand test is to be preferred for materials undergoing biological oxidation, it is not, itself, a good measure of the effect of liquors on sewage oxidation processes. One reason for the difference is that such processes go much nearer to completion than the B.O.D. test. Another is that preferential breeding of bacteria and other organisms occurs in the beds and sludges that are employed in sewage-disposal processes, and the improved types act more efficiently. These differences demonstrate that the effect of still waste or ammoniacal liquor on sewage cannot be evaluated by analysis alone but should be measured by actual trial under representative conditions.[265]

Principal Types of Sewage-Treatment Processes. Bacterial processes for sewage treatment vary widely, depending on such factors as the strength of the sewage and the volume of the stream into which the final effluent is discharged. Typical processes described by Buswell [267] will be briefly reviewed here. The first steps in general are screening to remove larger solid bodies, and settling in grit chambers to remove sand and gravel.

The sewage then enters settling tanks which are designed for removal of all remaining settleable solids. Many types of

265 Chapter 6 of ref. 11.

266 Parker, A., *Gas J.*, 179, 172–5 (1927).

267 Buswell, A. M., *The Chemistry of Water and Sewage Treatment,* Chemical Catalog Co., New York, 1928, 362 pp.

TABLE XXXII

Oxygen Consumption of Mixtures of Sewage and Still Wastes from Horizontal and Continuous Vertical Retorts [266]

| | Domestic Sewage | | |
	Strong	Medium	Weak
		Oxygen Consumed	
		parts per million	
No addition	150	100	50
1 percent of horizontal retort liquor added	189	139	89
2 percent of horizontal retort liquor added	227	178	129
1 percent of vertical retort liquor added	224	174	124
2 percent of vertical retort liquor added	297	248	199

settling tanks are used. In some, the sludge is drawn off, either periodically or continuously, to separate tanks for digestion. Other types, septic tanks, are built with sufficient capacity to allow the accumulation and digestion of the sludge under anaerobic conditions. Such sludge is not removed until digestion is complete.

The disturbing effect of the gaseous products from sludge digestion in septic tanks on the sedimentation has been avoided by use of two-story tanks, of which the Imhoff tank is an example. The sewage enters the upper chamber, and the sludge settles through slots at the bottom into the lower digestion chamber. The slots are so arranged as to baffle the gases produced in the digestion chamber and prevent their entering the upper chamber. Digested sludge alone is removed from the lower chamber, and settled effluent leaves the upper.

The liquid effluent from the settling tank carries 65 percent or more of the putrescible matter of the sewage. This organic matter is largely in colloidal form, although a portion is in solution, and some still in suspension. If further purification is necessary before discharge from the plant, the effluent is subjected to the action of bacteria in suitable bacterial beds or tanks.

In bacterial beds, or filters, as they are often called, purification takes place by contact of the effluent with the bacterial or mold growths which accumulate on the surface of the material with which the bed is filled. This may be gravel, crushed rock or slag, clinker, coke, or sand. The material is usually screened to a uniform size, which may vary from that of sand up to 2 or 3 inches or larger. The finer material furnishes more surface per cubic foot but becomes clogged more readily and requires more care.

The principal types of filters are trickling or sprinkling filters, contact beds, and intermittent sand filters. As the name implies, the liquor to a sprinkling filter is distributed over the surface of the bed and trickles down in contact with the jellylike growths. Two views of trickling filters are shown in Fig. 8. Contact beds are flooded from the bottom with the sewage and then drained after a period of contact. Intermittent sand filters operate much like sprinkling filters.

Bacterial purification in tanks utilizes what is known as the activated-sludge process. The clear effluent from sedimentation is mixed with a small proportion of activated sludge from previously treated sewage and run into aeration tanks. The
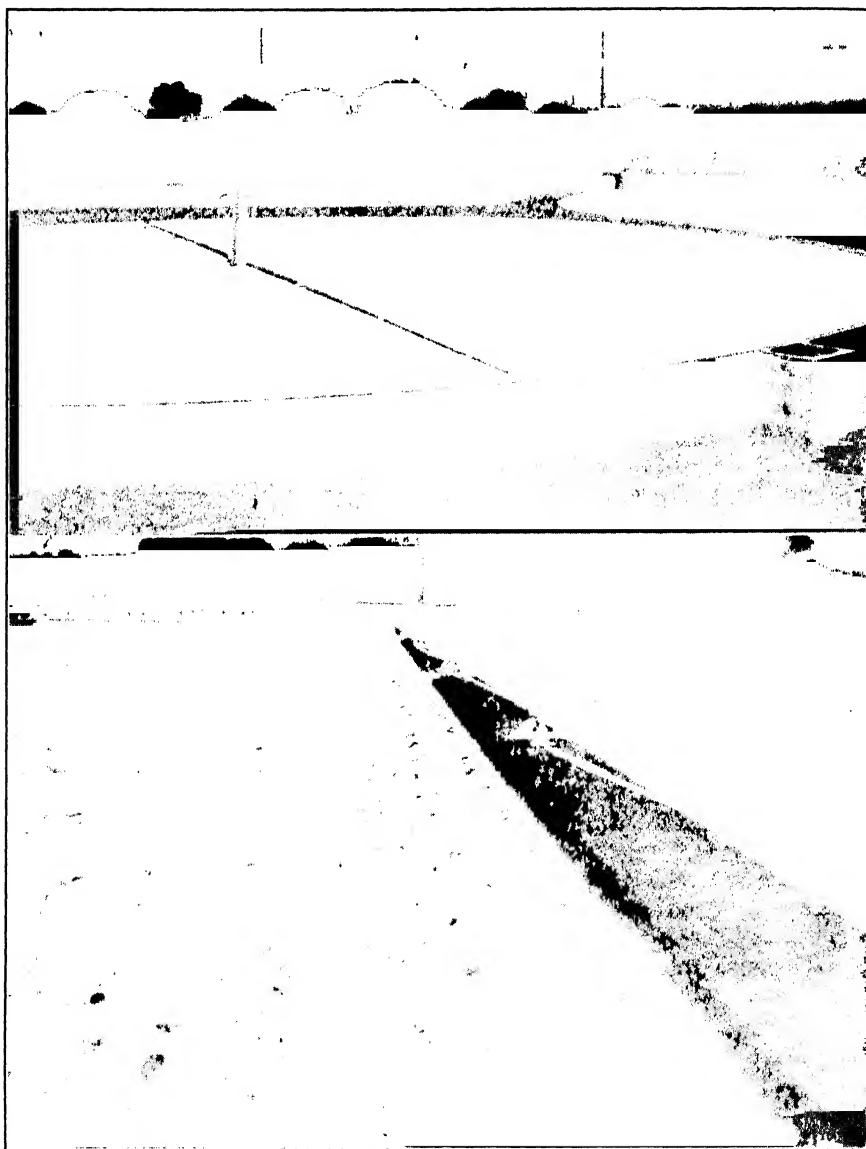
Fig 8   Two views of trickling filters   The lower view is a close-up showing the distribution of the sewage.   (Courtesy of Sewage Works Engineering.)

sludge consists of flocs of bacterial growth which, in contact with the organic matter under aerobic conditions, utilize a portion in growth and oxidize part to carbon dioxide and nitrate. After the necessary aeration period, the liquor passes to a sedimentation tank where sludge settles out, and the clear liquor is discharged. Activated-

should be efficiently separated from the liquor by filtration through beds of coke or other suitable material before admixture with the sewage since the tar carries large quantities of phenol and higher tar acids, which are extracted by the sewage, and since, in addition, the deposition of tarry matter on the bacterial beds, or other puri-
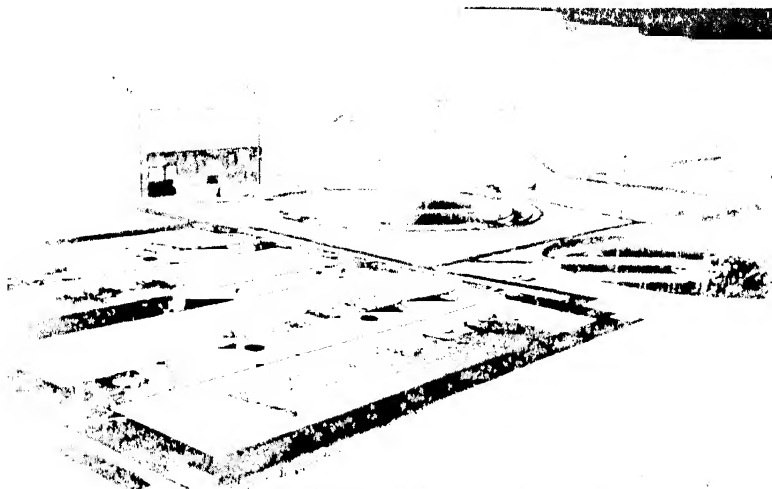
FIG. 9   Activated-sludge tanks for sewage treatment.   (Courtesy of Sewage Works Engineering.)

sludge tanks are shown in operation in Fig. 9.

Ammoniacal liquor and still waste have been treated in admixture with sewage by all these processes. Comprehensive investigations of the treatment of liquors from coke and gas plants in sewage-disposal works have been made by the Institution of Gas Engineers over a number of years, and the results of their work have been reported periodically by members of their Liquor Effluents and Ammonia Subcommittee. As summarized by Key,[268] the following requirements are essential to any successful treatment: (1) entrained tar

[268] Chapter 5 of ref. 11.

fication media, impairs their efficiency; (2) the liquor should be cooled—110° F is a satisfactory temperature at which to admix the liquor with the sewage; (3) the ratio of still waste to dry weather flow of sewage should remain relatively constant throughout the 24 hours (a storage tank of suitable size will serve to even out irregularities in operation); and (4) the discharge of still waste from the plant should be positively controlled by an orifice or series of orifices at constant head rather than by an adjustable valve.

Given these conditions, the difficulty of treating sewage containing waste liquor depends more than anything else, according

to Key,[268] on the proportion of liquor in the sewage. Hurley[269] also emphasized the importance of tar and oil separation, and proper regulation of the liquor flow.

In British practice, the amount of waste gas liquor usually varies between 0.2 and 0.5 percent of the amount of sewage, with an average proportion of 0.4 percent. Where ammoniacal liquor is discharged directly to the sewer, the average proportion is 0.3 percent.[268]

Effect of Liquors on Settling of Sewage. The investigations of the Institution of Gas Engineers have included studies of the effects produced on the various sewage-purification processes by the addition of gasworks liquors. No deleterious effect has been noted on the settling of crude sewage.[270]

Purification of Liquor on Sprinkling Filters with Sewage. Still waste in admixture with sewage has been purified successfully on bacteria beds. The pioneer work with this process was done by Frankland and Silvester[271] on a plant scale at Oldbury in 1907. The addition of waste liquor in the proportion of 9 percent of the sewage flow retarded the action of the bacteria but did not kill them. This proportion of waste could be satisfactorily purified by providing larger area of beds, giving triple contact, and permitting only a diminished flow of sewage onto the beds. The effluents from the beds were nonputrefactive and supported fish life. They were almost invariably free from thiocyanate.

In the same year, Radcliffe[272] reported that bacteria in the beds were destroyed

when the proportion of spent liquor in the sewage reached 3 percent. The toxic action was ascribed partly to thiocyanate. Addition of 1 percent of the waste liquor did not appear to retard bacterial action.

Laboratory tests made at the University of Illinois were described by Lenzing[273] in 1917. Gas-house wastes containing 0.2 to 0.43 gram per liter of phenol, when added to sewage in the proportion of 10 and even 15 percent, had no influence on the biochemical oxidation and had no inhibiting effect on the number of bacteria.

The results obtained with gas liquors in trickling filters, which have been published in the reports of the Liquor Effluents and Ammonia Subcommittee of the Institution of Gas Engineers,[274] have been summarized by Key. The response of sewage to treatment was not altered by any change brought about by gasworks liquors. Phenol and catechol added to sewage were oxidized easily by any bacterial bed dealing with normal sewage. Thiocyanate was dealt with successfully only by sewage-purification media that had become acclimatized to the presence of this substance; ammonium sulfate and carbon dioxide were the products of the oxidation. Usually, oxidation of the constituents of gasworks liquors proceeded to a certain point, then almost stopped, leaving what may be called an oxygen absorption residue. This residue

269 Hurley, J., *Sewage Purif.*, 1, 158–300 (1939).

270 Key, A., et al., *Inst. Gas Engrs., Commun.* 102 (1934), 52 pp.; *Trans. Inst. Gas Engrs.*, 84, 215 (1934–5); *Gas World*, 101, 449, 614–17 (1935); *Gas J.*, 208, 854–6, 520–3 (1934).

271 Frankland, P. F., and Silvester, H., *J. Soc. Chem. Ind.*, 26, 281–7 (1907).

272 Radcliffe, J., *Surveyor*, 30, 406 (1907).

273 Lenzing, C. W., *Univ. Illinois, Bull.* 15, Water Survey Series No. 14, 169–74 (1917).

274 Chapter 6 of ref. 11. Key, A., *Surveyor*, 81, 335–7 (1932); *Munic. Eng.*, 89, 301 (1932); *Gas J.*, 198, 83–4 (1932); *Gas World*, 96, 387 (1932); *Inst. Gas Engrs., Commun.* 77 (1933), 66 pp., 102 (1934), 52 pp., 123 (1935), 66 pp.; *Gas World*, 99, 425–7, 466–95 (1933), 101, 449, 614–7 (1934), 103, 889–90, 423–4, 439–40 (1935); *Gas J.*, 204, No. 3676 Suppl., 4–5; 506–10, 882–3 (1933), 208, 854–6, 520–3 (1934), 212, 476–82 (1935); *J. Roy. Sanit. Inst.*, 56, 484–501 (1936). Key, A., and Etheridge, W., *Surveyor*, 86, 29–30, 67 (1934). Happold, F. C., and Key, A., *Biochem. J.*, 31, 1323–9 (1937).

remained almost constant, even after prolonged treatment. It originated in tar-soluble bodies, other than phenols and catechol, although it might contain thiocyanate, and was greater for vertical- than for horizontal-retort liquor. Sulfide and thiosulfate were easily oxidized, although the maximum concentration tolerated was smaller than for phenol and thiocyanates.

If fixed ammonia was retained in the liquor, it might or might not be completely oxidized in the filters. With incomplete oxidation of ammonia, an increase in the B.O.D. might be observed, but the increased oxygen demand will occur mainly in the later stages of the B.O.D. test. These results indicated that higher tar acids, thiocyanate, and fixed ammonium salts should be kept as low as possible. Since thiocyanate was oxidized on the bacterial beds to ammonium sulfate, there is a double reason for keeping the concentration of this compound to a minimum.

The behavior of ammoniacal liquor on bacterial beds in admixture with sewage, the Institution of Gas Engineers [275] has reported, will be similar to still waste, with two exceptions: (1) the quantity of nitrite in the effluent might be much larger than normal and, since nitrite is attacked by permanganate, the oxygen consumption might be correspondingly increased; and (2) owing to the relatively high ammonia content of the liquor, not all the ammonia might be oxidized on the beds, which would increase the B.O.D. of the effluent correspondingly. Ammoniacal liquor in sewage added to the work required of a bacterial

bed system to a much greater degree than a corresponding amount of spent liquor.

The results on the performance of biological filters, which have been reported by a number of other investigators, will be briefly described. In general, the addition of less than 1 percent gas liquor to sewage has not exerted a deleterious effect on bacterial filters. At Motherwell, raw gasworks liquor after filtration and dilution was discharged into the sewers. The diluted raw liquor had an oxygen absorption of 3,500 parts per million and contained about 3 grams per liter of ammonia. According to McDonald,[276] this ammonia acted as an antiseptic on the filters, and the liquor was probably insufficiently diluted with sewage. Gas liquor containing both ammonia and hydrogen sulfide, when admixed with sewage to concentrations of approximately 0.3 percent, was satisfactorily purified at Buxton. In the opinion of Oliver,[277] any appreciable increase above this limit would have necessitated a preliminary purification of the liquor.

Scott [278] considered that 0.35 percent of spent gas liquor in sewage was very serious. At Bury, this proportion of spent liquor, which had an oxygen demand of 9,310 parts per million, led to a rapid deterioration in quality of the effluent from the plant followed by a gradual partial recovery. A later addition of gas liquor to the sewage caused the percolating beds to lose most of their bacterial growth.

Wossnessensky and Aron [279] found that effluents from brown-coal carbonization

[275] Chapter 6 of ref. 11. See also *Inst. Gas Engrs., Commun.* **102** (1934), 52 pp.; *Trans. Inst. Gas Engrs.,* **84,** 215 (1934–5); *Gas J.,* **208,** 354–6, 520–3 (1934); *Gas World,* **101,** 449, 614–17 (1935). Key, A., and Etheridge, W., *Inst. Sewage Purif. (Engl.),* **1936,** Pt. II, 278–300; *Surveyor,* **90,** 603–5 (1936); *Munic. Eng. Sanit. Rec.,* **98,** 606 (1936). *Engineering,* **14,** 682 (1936).

[276] McDonald, A., *Gas J.,* **203,** 623–7 (1933); *Gas World,* **99,** 246 (1933).
[277] Oliver, F., *Surveyor,* **85,** 55–6 (1934); *Munic. Eng.,* **93,** 103 (1934).
[278] Scott, W., *Surveyor,* **85,** 327, 333 (1934); *Munic. Eng.,* **93,** 316 (1934).
[279] Wossnessensky, D., and Aron, S., *Zhur. Prikl. Khim. Leningrad,* **7,** 926 (1934); *Dept. Sci. Ind. Research (Brit.), Water Pollution Research, Summary Current Lit.,* **8,** 213 (1935).

could be purified on contact beds. By slowly accustoming the filters to the mixture, concentrations of 70 parts per million of phenol could be eliminated. The experience of Wishart[280] with phenols was similar. They were readily oxidized, once the plant was accustomed to them. Ammonium compounds, he considered, were the only constituents of gas liquor really beneficial to sewage treatment, because they supplied the nitrifying bacteria with easily assimilable nitrogen. Sulfides might cause trouble, unless the sewage was maintained alkaline.

Ott,[281] on the other hand, considered ammonia and phenol the most toxic substances in waste liquor but reported that ammonia below 1 part per million was not harmful.

In experimental work on the purification of sewage containing gas liquor in trickling filters, Garner and Wishart[282] found the filters to have an optimum efficiency when treating concentrations of gas liquor between 0.5 and 1 percent. Within this range, the filters would handle the mixture at a uniform rate of 70 gallons per cubic yard per 24 hours, with a reduction in phenol content of 60 to 70 percent. More than 1 percent of gas liquor was definitely harmful to the process of purification. Part of the ammonia compounds from the liquor were nitrified during the biological filtration. Slater[283] discussed his experience with gas liquor in city sewage. Half a percent seriously interfered with the operation of the plant. After the admission of the liquor to the sewage was controlled

and the mixture subjected to a sand filtration, the liquor was purified successfully. Mohlman[284] dosed experimental sand filters with a still waste-sewage mixture intermittently at the rate of 100,000 gallons per acre per 24 hours. He found that phenol concentrations up to 25 to 35 parts per million did not cause serious interference with the biology of intermittent sand filtration.

In connection with his survey of the River Tees, Southgate[285] found that 0.13 part per million of phenol did not interfere with the biological oxidation of sewage, and was itself oxidized. p-Cresol was apparently more readily oxidized than phenol. The rates of oxidation of tar acids were increased by increasing concentrations of sewage. Cyanides in concentrations of 0.001 to 0.01 part per million partly inhibited the biological oxidation of sewage, although the number of bacteria capable of growing in agar at 20° C was greater in sewage containing 0.01 part per million of CN than in sewage alone.

Effect of Liquors on Activated Sludge. Positive results on the purification of ammoniacal liquors and wastes with activated sludge have also been obtained. Uglow[286] found that activated sludge from household waste had an outstanding specializing action for the destruction of such aromatic compounds as phenol. Concentrations as high as 1,800 parts per million could be destroyed, but cresol and p-naphthol were less easily attacked. The destructive action could be increased by gentle aeration.

Heiduschka and Göbel[287] investigated

[280] Wishart, J. M., *Surveyor,* **87,** 309 (1935).

[281] Ott, E., *Schweiz. Ver. Gas- u. Wasserfach. Monats-Bull.,* **16,** 45 (1936) ; *Brennstoff-Chem.,* **17,** 189 (1936).

[282] Garner, J. H., and Wishart, J. M., *West Riding of Yorkshire Rivers Board Rept. 174* (1936), 26 pp.

[283] Slater, J., *Surveyor,* **81,** 199 (1932) ; *Munic. Eng.,* **89,** 98 (1932).

[284] Mohlman, F. W., *Am. J. Pub. Health,* **19,** 145-56 (1929).

[285] Southgate, B. A., *Chemistry & Industry,* **52,** 1-4T (1933).

[286] Uglow, W. A., *Z. Hyg. Infektionskrankh.,* **111,** 511-30 (1930) ; *Chem. Abs.,* **25,** 758 (1931).

[287] Heiduschka, A., and Göbel, J., *Chem.-Ztg.,* **56,** 589-90 (1932).

the action of phenols on a mixture consisting of a freshly aerated activated sludge and a nutrient solution containing urea, ammonium phosphate, and calcium and magnesium chlorides. With additions of phenol and *p*-cresol, a decrease in the bacterial number first occurred at concentrations of 8.2 and 4.0 grams per liter, respectively.

The work of the Institution of Gas Engineers on activated sludge has also been summarized by Key.[274] Two important differences between the purification of sewage in a bacterial bed and with activated sludge were found:

1. The purifying organisms in a bacterial bed were segregated to a certain extent, those at the top being in perpetual contact with and adapted to the crude sewage, and those lower down continually dealing with partially purified material. In activated sludge, on the other hand, the organisms dealt with the sewage at all stages of oxidation. The bacteria of activated sludge might thus be more sensitive to constituents of the liquor than those in the bacterial beds.

2. In many cases, with activated sludge it was not necessary to oxidize the ammonia in order to obtain an effluent which met the usual requirements. If it were not for the slight toxic effect exerted by the compounds in the ammoniacal liquor on the bacteria in the activated sludge, an ammoniacal liquor could probably be treated with activated sludge as easily as a spent liquor.

The order of oxidizability of the compounds in the liquors was the same with activated sludge as in bacterial beds. Generally, an average dose of spent liquor could be treated by activated sludge. A slight delay, which might occur in the first stages of the treatment, disappeared as the liquor was purified. Ammoniacal liquor

had a greater retarding effect initially, a greater final effect on the oxygen absorption, and an appreciable effect on the B.O.D.

The tests of Copeland [288] at Milwaukee, Wis., indicated that the activated-sludge process would remove the taste of phenolic compounds from sewage containing as much as 2 percent of the ammonia liquors originating in coke and gas plants. The number of bacteria in the sludge was increased, but the quality of the sludge was not injured.

From his studies on the biological purification of ammonia still waste, Mohlman [289] concluded that the activated-sludge process would handle 30 to 40 parts per million of phenol from ammonia still wastes without seriously impairing the quality of the effluent. Phenolic destruction appeared to be accomplished by aerobic bacteria; anaerobes seemed unable to decompose phenols unless a very long period of contact was permitted. Reinoculation, using 10 percent inoculum of a previous sludge, accelerated oxidation and reduced the time of treatment by 40 percent. Phenolic wastes oxidized much more rapidly at higher temperatures. At 20° C, the phenol content was decreased from 2.5 to 0.1 part per million in 3.4 days, whereas at 10° C a similar decrease required 7.4 days. The decreased rate of oxidation at lower temperatures explains why chlorophenol tastes are more prevalent in winter than in summer.

Brown [290] found that still waste diluted to 10 volumes and aerated in an activated-sludge system was more than 90 percent purified in 7 hours, as measured by the

[288] Copeland, W. R., *Milwaukee Sewage Comm., 7th Annual Report* (1920) ; *Chem. Abs.*, **16**, 2002 (1922).
[289] Mohlman, F. W., *Am. J. Pub. Health*, **19**, 145–56 (1929).
[290] Brown, R. L., *Am. Gas Assoc. Monthly*, **8**, 211–14, 240, 254, 279–82, 302 (1926).

oxygen consumption. Phenols could not be detected in the effluent.

Nolte and his colleagues [291] discovered that phenolic wastes could be successfully treated by the activated-sludge process, with the addition of phosphate for nourishment of the bacteria. No addition of domestic sewage was necessary.

Activated sludge is much more susceptible to tar than are the bacterial growths on a trickling filter. If an ammoniacal liquor is to be treated in an activated-sludge plant, the tar particles must be efficiently separated.[292]

Effect of Liquors on Imhoff Tank Operation. The action of phenolic wastes upon the sanitary sewage and sludge digestion in Imhoff tanks at Rochester, N. Y., was reported by Ryan and coworkers.[293] They added ammonia still waste to sewage in the proportion of 0.1 percent, without ill effects on the operation of the Imhoff tanks. The total phenol concentration in the mixture was 5 parts per million. The safe dilution for the still waste appeared to lie below a waste-sewage ratio of 1 to 166. Only a portion of the phenol was destroyed in the Imhoff tanks. Although no change in the physical characteristics was found, the sludge was better stabilized and more completely digested. Marked increases in the numbers of both the aerobic and anaerobic bacteria population were noted.

Bacterial Filters for Still Waste. Purification of coke-plant effluents in admixture with sewage has led to the investigation of similar processes designed exclusively for treatment of these liquors. Fowler and his collaborators [294] studied the purification of spent gas liquors by bacterial action without admixture with sewage. The filters flow of the mixture over the beds was 100 were first matured by treatment with sewage and were afterwards employed in the treatment of spent gas liquor diluted with filters showed 80 percent purification of the diluted liquor, the purified effluent was water. As soon as the effluent from the used in place of water as the diluent. One volume of still waste was diluted with 9 volumes of treated effluent, and the rate of gallons of diluted liquor, equivalent to 10 gallons of the original still waste, per cubic yard per day. The purification obtained was 92 to 98 percent, calculated on the oxygen consumption of the undiluted liquor.

A system of this design was installed at the Bradford Corporation Chemical Works, England, about 1908. The filters were constructed of graded clinker. The degree of purification obtained during the first few years was similar to that obtained in the experimental work, but, owing to the higher oxygen-consumed value of the still waste (over 7,000 parts per million), the dilution was 1 in 20, and the rate of flow, 80 gallons of diluted liquor per cubic yard per day. It was operated for more than 10 years but was expensive in both capital and operating costs. From his study of it, Key concluded that bacterial oxidation is best carried out at a sewage-disposal works, where a high degree of waste dilution is possible.[295]

291 Nolte, E., et al., *Wasser*, 8, Pt. 1, 126–47 (1934) ; *Chem. Abs.*, 29, 4497 (1935) ; Brit. Pat. 435,363 (1935). Nolte, E., *Deut. Landeskultur-Ztg.*, 7, 14 (1938) ; *Chem. Abs.*, 33, 4717 (1939).

292 Hoak, R. D., private communication, 1941.

293 Ryan, W. A., *Am. J. Pub. Health*, 19, 155–6 (1929). Ryan, W. A., and Shnidman, L., *Penna. State Coll., School Eng., Tech. Bull.*, 10, 27–52 (1930). Shnidman, L., and Bowman, L. B., *Gas Age-Record*, 61, 626–8, 634 (1928).

294 Fowler, G. J., Arden, E., Lockett, W. T., *J. Soc. Chem. Ind.*, 30, 174–9 (1911) ; *Proc. Roy. Soc. (London)*, 83B, 149–56 (1911). Fowler, G. J., and Holton, A. L., *J. Soc. Chem. Ind.*, 30, 180–1 (1911). Fowler, G. J., and Shepard, S. W., *ibid.*, 30, 181–4 (1911).

295 See pp. 77–8 of ref. 11. Monkhouse, A. C., *Gas J.*, 170, 103–4 (1927), 182, 1016–8 (1928).

In their experimental work, Fowler, Arden, and Lockett [294] succeeded in isolating special organisms which oxidized phenol. Horowitz-Wlassowa [296] took issue with Fowler and later investigators in regard to the importance of bacteria for the destruction of phenol on bacterial filters. In his opinion, phenol exerts a toxic action on bacteria, and the purification is really a physical-chemical oxidation by the oxygen in the air which is admitted to the beds. The bacteria, *B. helvolum*, isolated by Fowler, he stated, were an ordinary water type without marked biochemical action.

Wilson [297] conducted experiments on mixtures of sewage and still waste. The filter was fed with crude domestic sewage for a few weeks, then for a week or so with sewage containing about 8 percent gas liquor, at the end of the period reverting to domestic sewage. The rate of filtration was slow, 15 gallons per cubic yard of filtering material per 8-hour day. At this rate the oxygen-consumed value was reduced by 90 to 95 percent and the thiocyanate by 95 percent. The results, in general, showed that, so long as the rate of flow did not exceed this amount, sudden changes in composition of the influent did not materially disturb the operation of the filter.

Lowe and Ely [298] described biological filters in which animal charcoal was used. The charcoal, in addition to forming a support for the bacteria, also took up free ammonia, tar oils, and phenols. The charcoal could be heated to drive off ammonia.

Brown [299] prepared bacterial beds by mixing peat or other humus material with coke and inoculating with aerobic bacteria from sewage sludge. Still waste was diluted with previously purified effluent until it represented 10 to 15 percent of the mixture and was passed through the bed at the rate of 10 to 20 gallons of crude still waste per cubic yard of filter contents per 24 hours. A phenol concentration of 100 to 200 parts per million in the mixture to the filters, but not in excess of 300 parts per million, was recommended. Best results were secured at temperatures of 20 to 25° C. An experimental filter of this type ran successfully and continuously for a year, according to Leitch.[300] Similar filter beds of lignite have been described by Davis and Semenow.[301]

In his surveys of methods for disposal of still wastes, Sperr [302] found that the bacterial filter, although giving good results, required an excessive ground area, and the cost of installation was high. Powell [303] suggested that bacterial filters might be used for removal of the last traces of phenol left in the liquor after removal of the major portion by other processes.

The phenol content of the waste liquor from coke-oven plants in the Emscher region of Germany has been so great as to seriously affect the Rhine. Analyses of liquors were as follows: [304] phenols, calcu-

U. S. Pat. 1,437,894 (1922). Dieterle, E. A., and Semenow, S. D., U. S. Pat. 1,328,256 (1919); Brit. Pat. 152,356 (1920). Koppers Co., Fr. Pat. 533,922 (1922); *Chem. & Met. Eng.*, 28, 272 (1923).

296 Horowitz-Wlassowa, L., *Gas- u. Wasserfach*, 73, 275–8 (1930). Bach, H., and Horowitz-Wlassowa, L., *ibid.*, 73, 711 (1930).

297 Wilson, H. M., *J. Roy. San. Inst.*, 33, 522 (1912); *J. Gas Lighting*, 119, 388–9 (1912); *Chem. Trade J.*, 51, 135–6 (1912). Hooper, H. R., *Munic. Eng. Sanit. Record*, 8, 90–1 (1928).

298 Lowe, F. R., and Ely, B., Brit. Pat. 19,074 (1910).

299 Brown, R. L., Brit. Pat. 161,976 (1921);

300 Leitch, R. D., *U. S. Pub. Health Service, Pub. Health Repts.*, 40, 2021–6 (1925).

301 Davis, H. S., and Semenow, S. D., U. S. Pats. 1,323,251 (1919), 1,437,401 (1922); Brit. Pat. 139,159 (1919).

302 Sperr, F. W., Jr., *Am. J. Pub. Health*, 19, 901–7 (1929).

303 Powell, A. R., *Proc. Am. Gas Assoc.*, 1929, 928 33; *Gas Engr.*, 47, 32–3, 34 (1930).

304 Bach, H., *Gas- u. Wasserfach*, 69, 912–5, 947–51 (1926). Prüss, M., *ibid.*, 72, 791–801 (1929); *Gas J.*, 184, 404–7 (1929).

lated in parts per million as C_6H_5OH, 1,300 to 2,700; thiocyanate, 90 to 260; nitrogen in NH_3 and organic compounds (not including cyanides), 160 to 350; sulfur in sulfates, sulfides, and organic compounds, 260 to 1,400; free lime, as CaO, 400 to 900; and potassium permanganate for oxidizing organic matter, 10,000 to 40,000.

Biological methods of purification were studied by the Emscher Commission, and a bacterial filter was devised by Bach.[304, 305] The Emscher filter consisted of a rectangular tank filled with walnut-size clinker, which served as a support for the organisms. The waste liquor was diluted with previously purified effluent from the bed and admitted at one end of the tank. In its passage through the filter to the exit at the other end, the liquor was diverted up and down through the clinker by suitable baffles. The necessary oxygen was supplied by the admission of air from inlet pipes laid in the bottom of the tank. At one plant, 8 cubic feet of air per gallon of effluent was used. A temperature of 20 to 25° C was recommended. Constant addition of household sewage was essential, and the proper dilution and alkaline conditions had to be maintained. Up to 10 percent

of effluent in the feed to the beds did not interfere with the bacterial processes. In a contact time of 2 hours, practically all the phenol and thiocyanate were destroyed.

Results obtained in an Emscher filter are shown in Table XXXIII.[304] Such a filter would purify approximately 100 gallons per cubic yard of packing material per 24 hours. On account of the large volumes of liquor to be treated, the plant cost and ground area required were high and the process did not prove economical. Bach[305] stated that the cost of purifying the waste from lignite carbonization in the Emscher filters was even greater than for that from bituminous coal.

Hurley[306] described experiments on the operation of a filter consisting of graded coke, mixed with matured clinker from a sewage filter. Crude gas liquor was diluted to 7 times its volume and passed through the bed. Large proportions of both phenol and thiocyanate in the liquor were eliminated.

Use of Precipitants for Treatment of Sewage Containing Ammoniacal Liquor. Chemicals are added to sewage in order to precipitate suspended matter,[307] and interest in this method of treatment is increas-

305 Bach, H., *Angew. Chem.*, **39**, 1093–8 (1926); *Wasser u. Gas*, **20**, 393 (1930); *Wasser u. Abwasser*, **27**, 254 (1930); U. S. Pat. 1,745,-397 (1930); Ger. Pat. 426,422 (1930).

306 Hurley, J., *Contract Record Eng. Rev.*, **41**, 1355, 1384 (1930).

307 See pp. 50–3 of ref. 11. *Inst. Gas Engrs., Commun.* **142** (1936), 87 pp.; *Trans. Inst. Gas Engrs.*, **86** (1936–37).

TABLE XXXIII

PURIFICATION OF STILL WASTE IN AN EMSCHER FILTER [304]

	Raw Waste Liquor after Separating Lime	Diluted Waste	Purified Effluent
		parts per million	
Phenols as C_6H_5OH	1,300–2,100	220–320	15–40
Thiocyanate as CNS'	100–160	15–45	0–6
Permanganate demand	11,000–38,000	2,000–2,600	650–850
Biochemical oxygen demand	>1,000	....	<1,000
Organic and sulfide sulfur	300–450	50–150	10–20

ing. Since ammoniacal liquors contain very little suspended matter, their oxygen-absorption value will be unaffected by the addition of precipitants. Ferric chloride and lime, precipitants frequently employed, are, however, liable to produce intense colors in the presence of even dilute solutions of ammoniacal liquors.

The effect of lime is to increase the alkalinity of the liquor and, in consequence, the rapidity of oxidation of the higher tar acids, the products being highly colored. Ferric chloride reacts with higher tar acids to produce colored bodies of unknown composition. It also reacts with sulfide, producing ferrous sulfide which, in the presence of sewage, remains in colloidal solution as a black material.

Effect of Liquor on Development of Odors in Sewage. Sewage is said to become "septic" when it develops odors. This change is due to biochemical action out of contact with air, which results in the reduction of sulfur compounds in the sewage to hydrogen sulfide. Spent liquor in concentrations of 0.4 to 0.5 percent does not appear to affect the rate at which a sewage becomes septic, but ammoniacal liquor in excess of 0.3 percent retards it somewhat.[307] This was ascribed by Happold and Key[308] to a mild antiseptic action which is more apparent in the absence than in the presence of air. O'Shaughnessy[309] found that sewage samples kept in the laboratory remained inoffensive when they contained 0.5 percent gas liquor.

Chlorine Treatment of Sewage Containing Liquor. Septicity of sewage has been reduced in a number of cases by the application of small doses of chlorine. This addition does not sterilize the sewage but is sufficient to delay anaerobic action. The Institution of Gas Engineers[307] has found that the addition of gas liquor greatly increases the amount of chlorine required to effect complete sterilization of the sewage but exerts scarcely a measurable influence on the amount required for the destruction of hydrogen sulfide.

METHODS FOR IMPROVEMENT IN LIQUOR PRODUCTION

The principal methods for improvement in the production of ammonia liquor are as follows: (1) Reduction in the volume of liquor. In general, the smaller the volume of liquor, the more easily is it disposed of. This does not necessarily hold when the concentration of the constituents increases with decrease in the volume. (2) Change in the byproduct-recovery process to reduce or eliminate certain objectionable constituents from the liquor, the removal of which is otherwise difficult. (3) Treatment of the liquor after production for the removal of constituents otherwise difficult to eliminate.

REDUCTION IN THE VOLUME OF AMMONIACAL LIQUOR

In a coke plant utilizing the semi-direct sulfate-recovery process, the volume of the aqueous condensates from the gas can be reduced only by drying the coal before carbonization. This is usually impracticable, and the water of constitution of the coal cannot be eliminated.

In indirect process plants, 40 to 60 percent of the ammonia is generally removed in the gas cooling stages.[310] The balance of the ammonia must be removed in the washers. The volume of the washer liquor may be reduced in one of the following ways: (1) increase in the efficiency of the

308 Happold, F. C., and Key, A., *J. Hyg.*, **32**, 573–80 (1932).

309 O'Shaughnessy, F. R., *Gas J.*, **188**, No. 3472 (1929) ; *Inst. Gas Engrs., Suppl.*, 64–70 (1929).

310 Plenz, F., *Gas- u. Wasserfach*, **66**, 97–9 (1923) ; *Am. Gas J.*, **119**, 29–32 (1923).

ammonia scrubbers, either by means of an improved design or by operating them more efficiently and at a lower temperature; or (2) replacement of fresh water by liquor low in free ammonia.

The liquors condensed during the cooling of the gas are progressively weaker, the higher the temperatures at which they are produced. It, therefore, may be possible to find liquors from the first stages of condensing the gas, which may be sufficiently low in free ammonia to substitute for all or part of the fresh water.[311] Henshaw and Cooper [312] reported that an enrichment of some 20 percent in the weak liquor is to be expected when the hot condensate from the condenser is used in the scrubbers. The condensate is free from scale-forming compounds, sometimes present in water, which would accumulate in the scrubbers.

Liquor from which the free ammonia has been stripped has also been used.[313] Whatever the source, the liquor should be cooled to the scrubber temperature before use and, in regulating the addition, allowance should be made for any residual ammonia. Reuse of liquor in the scrubbers does not necessarily reduce the concentration of constituents other than ammonia, because thiocyanate and thiosulfate will build up at a rate equal to that with fresh water.[314] The use of limed still waste after cooling would be undesirable, because of the deposition of calcium carbonate scale in the scrubbers. Fillunger found that the concentration of fixed salts did not build up in the recirculated liquor, because they were decomposed by the organic bases.

The use, in the scrubbers, of gas condensate from which the ammonia had been removed by contact with a portion of the hot gases has been patented by Tyrer.[315] After removal of the free ammonia, the liquor was cooled and substituted for the wash water in the scrubbers.

The strength of the final liquor from ammonia scrubbers was improved by de Voogd and van der Linden,[316] who discarded the liquor from the next to the last compartment to the sewer. Only 1 percent of the ammonia was lost in this discard. Such a process would not reduce the total effluent from the plant.

Gas Refrigeration. By cooling gas to 0° C, a concentrated ammonia liquor can be produced. An analysis of such a liquor in grams per liter was:[317] total ammonia, 96.3; volatile ammonia, 96.0; carbon dioxide, 129.0; sulfide as S, 4.9; and hydrogen cyanide, 0.3. Other data on the operation of two German plants in which the gas was cooled to 0 to −5° C by means of refrigerated ammonia liquor have also been reported.[318] A spray of 4 to 6 percent ammonia liquor was used to cool the gas leaving the primary coolers. Removal of the ammonia was completed by washing with water at approximately 0° C in a second scrubber, in which a liquor containing 2 to 3 percent of ammonia was produced.

[311] Chapter 8 of ref. 11. Hollings, H., *Trans. Inst. Gas Engrs.*, **77**, 522 (1927–28). Gas Light and Coke Co., Hollings, H., Pexton, S., and Hutchison, W. K., Brit. Pat. 334,619 (1929).

[312] Henshaw, D. M., and Cooper, C., *Gas J.*, **230**, 564–5, 569–72 (1940); *Gas World*, **112**, 306–7 (1940).

[313] Grossman, J., *J. Soc. Chem. Ind.*, **25**, 411–3 (1906). Tokin, L., *J. Chem. Ind.* (*U.S.S.R.*), **2**, 319–29 (1927); *Chem. Abs.*, **21**, 3730 (1927). Muhlert, F., *Brennstoff-Chem.*, **13**, 350–2 (1932). Tran, A., *Gas J.*, **226**, 472–4 (1939).

[314] Fillunger, A., U. S. Pat. 865,769 (1906); Ger. Pats. 209,847, 215,533 (1906).

[315] Tyrer, D., and Imperial Chemical Industries, Ltd., Brit. Pat. 322,049 (1928).

[316] De Voogd, J. G., and van der Linden, A., *Het Gas*, **57**, 70–6 (1937).

[317] Lenze, F., and Rettenmaier, A., *Gas- u. Wasserfach*, **74**, 1169–72 (1931).

[318] Lenze, F., Ger. Pats. 457,264 (1928), 482,- 880 (1929). Stoll, *Gas- u. Wasserfach*, **73**, 1102–4 (1930). Steding, F., *ibid.*, **75**, 164–9 (1932). Muhlert, F., *Brennstoff-Chem.*, **13**, 350–2 (1932). Thyssen'sche Gas- u. Wasserwerke, Ger. Pat. 583,417 (1933).

According to Pippig,[319] if the concentration of the liquor from the first scrubber was boosted to 14 percent ammonia, a hard deposit of ammonium carbonate was formed. With a maximum concentration of 12 percent ammonia no deposit formed and 82 percent of the ammonia in the gas was removed in the first scrubber.

Use of Acids. In the scrubbing of horizontal-retort gas, the primary condensate contains a low concentration of carbon dioxide. If carbon dioxide from some suitable source is added to this liquor before introduction into the scrubbers, its ammonia vapor pressure will be reduced.[320]

In English practice, lead-lined acid scrubbers have been used for recovery of the ammonia which would be lost when the water to the scrubbers was reduced. An ammonium sulfate liquor containing about 4 percent free sulfuric acid was circulated through such a scrubber, and fresh acid additions were continued until the ammonium sulfate content had risen to about 35 percent. The concentrated solution was then sent to the saturators.[321] The acid scrubber should be followed by an efficient alkali washer. Such acid scrubbers have been used for removal of all the ammonia from the gas after the condensers.[322]

Partial Evaporation of Liquor in Hydraulic Mains. The cooling of the hot gases from the ovens in the standpipes and hydraulic mains by evaporation of a portion of the circulated flushing liquor has been described. If the additions of water to this cooling liquor are limited merely to

replacement of the portion evaporated with no withdrawal, it is obvious that the concentration of nonvolatile impurities in the liquor will increase, particularly the ammonium chloride. The concentration of chlorides may be held substantially constant by withdrawing portions of the liquor from circulation periodically. Such withdrawals can result in a much smaller volume of flushing liquor in which the chloride, other inorganic salts, and some of the organic matter have been concentrated.

Becker[323] concentrated flushing liquor in a closed circuit until the salts built up to 10 percent. The liquor was then limed and distilled with indirect steam. From the still, a 40 percent solution of calcium chloride was obtained, which could be sprayed on coal and coke to allay dust.

The objections to the closed-circuit flushing system are as follows: (1) The tar which separates in contact with the liquor contains a higher concentration of chloride.[324] This may prove objectionable in subsequent handling or distillation. (2) The condensate from the primary cooler has still to be disposed of: separate equipment is required for recovery of the free ammonia which it carries, although liming of this liquor should not be necessary.

Concentration of Liquor in Vertical Retorts. The ammoniacal liquor from vertical retorts has been concentrated by using it for cooling the coke from the retorts. The liquor, preheated if possible, is pumped through sprays into the coke boxes. In cooling the coke, the liquor is heated, and some ammonia, volatile impurities, and steam pass upwards into the retort. The hot concentrated liquor is then sent to an ordinary free ammonia still, in which distillation is completed.

[319] Pippig, H., *Gas- u. Wasserfach*, **77**, 346–9 (1934).

[320] See pp. 65–6 of ref. 11. *Inst. Gas Engrs., Commun.* **19**, 31 (1930) ; *Trans. Inst. Gas Engrs.*, **80**, 268 (1930–31).

[321] Parrish, P., *Chem. Age (London)*, **11**, 208–9 (1924). Moon, P. G. G., *Gas J.*, **170**, 117–22 (1925). Bailey, T. L., *ibid.*, **171**, 385–6 (1925), **172**, 656–9 (1925).

[322] Parker, A., *Gas J.*, **179**, 173–5 (1927).

[323] Becker, J., U. S. Pat. 1,747,616 (1930).

[324] See pp. 67–8 of ref. 11.

The gases from the still, including steam, ammonia, carbon dioxide, phenol, and other impurities, are introduced into the base of the retorts. Here the ammonia is cracked to produce nitrogen and hydrogen; the phenols are also decomposed. Some of the steam and carbon dioxide react with the coke, but the fate of the hydrogen sulfide has not been determined.[325] The spent liquor from the still should be smaller in volume than usual and contain less phenol.

IMPROVEMENT IN COMPOSITION OF AMMONIACAL LIQUOR DURING PRODUCTION

Efforts have been made to control the production of ammoniacal liquors in such ways that solution of objectionable compounds will be reduced. In American practice, factors other than liquor quality usually control the composition, and the operator's influence proves very slight.

Reduction in the Content of Polyhydric Phenols. Production of an ammoniacal liquor with the minimum content of polyhydric phenols is always desirable, since these compounds give rise to colors and increase the oxygen absorption of water into which the liquor is discharged. Carbonization in horizontal retorts results in the formation of liquors containing relatively small quantities of the higher tar acids. Vertical-retort liquors, on the other hand, often contain much higher concentrations of the color-producing bodies. The difference is illustrated by analyses of liquors from the different parts of two byproduct-recovery systems, Table XXXIV.[326]

Higher tar acids, in contrast to monohydric phenols, according to Key,[327] are not volatile in steam; normally, therefore,

TABLE XXXIV

OXYGEN ABSORPTION OF LIQUORS FROM HORIZONTAL AND FROM VERTICAL RETORTS [326]

Liquor from	Retort House ppm	Atmospheric Condensers ppm	Scrubbers ppm
Horizontal retorts	1,200	1,500	150
Vertical retorts	4,250	2,250	250

they tend to condense with the tar and not with the liquor. If, however, tar and liquor condense at the same time, or if they are subsequently brought into intimate contact with each other, higher tar acids are transferred from tar to liquor until equilibrium is reached. In order to avoid this transference, it is necessary to prevent their contact.

Intimate contact of liquor and tar promotes the extraction of oxygen-absorbing substances, including color-producing bodies, by the liquor. Bailey[326] found that free ammonia favored the emulsification of liquor with tar when the two were shaken together; fixed salts, on the other hand, had a contrary effect. The effect of time of contact on the extraction of organic matter from tar which was stored in contact with liquor was shown by the following oxygen-absorption values: liquor stored 5 weeks in contact with tar and frequently agitated, 9,000; liquor distilled practically as made, 5,000; and liquor stored for 4 weeks with tar, 8,500 parts per million, respectively.

Intimate contact between tar and liquor in a liquor flushing system cannot be avoided if the liquor is circulated, according to Key.[327] If the liquor from the condensers is combined with the liquor circulated to the collecting main, the entire production of liquor will be contaminated with higher tar acids. Contact of tar and liquor in condensers and scrubbers can be reduced by use of efficient tar extractors on the

325 See p. 69 of ref. 11. Prater, T. H., *Trans. Inst. Gas Engrs.*, **81**, 233 (1931–32).

326 Bailey, T. L., *Ann. Repts. Alkali, &c., Works*, **61**, 16–21 (1925).

327 See pp. 70–1 of ref. 11.

hot, crude gas before the liquor begins to condense. In experiments at Hinchley, England, the heavy tar was almost completely separated from the gas with an electrostatic tar separator, located before the condensers. A marked reduction in the polyhydric phenol content of the liquor resulted; oxygen absorption decreased from 1,400 to 1,700 to 38 parts per million. The concentration of monohydric phenols increased.[328] At another plant, a cyclone tar separator removed 84 percent of the heavy tar from the gas before the condensers. This resulted in a 21 percent reduction in the oxygen absorption of the still waste.[328]

Reduction of Thiocyanate and Thiosulfate Content of Liquors. It has been shown that both thiosulfates and thiocyanates are oxidation products of ammonium sulfide. The extent to which both these reactions take place during liquor production is governed by:[329] (1) the oxygen content of the liquor, which in turn is controlled by the oxygen content of the gas or other atmosphere with which the liquor is in contact; (2) the time of contact between the liquor and the gas or air, since the reactions proceed relatively slowly; (3) the sulfide content of the liquor; and (4) the cyanide content of the liquor. The oxygen content of the gas may be held to a minimum by keeping the retorts tight and by maintaining a pressure on them. Air for oxide box revivification should be introduced into the byproduct-recovery apparatus at a point after the ammonia scrubbers.[329, 330]

The time of contact between gas and liquor in ammonia scrubbers varies considerably; it is much greater with tower scrubbers than with rotary scrubbers, and the tower scrubbers have been found to yield a liquor of higher thiocyanate and thiosulfate content.[329] The sulfide content of ammoniacal liquor is controlled with difficulty. Key[329] stated that in semi-direct process plants with indirect-type, secondary condensers, little or no sulfide is removed from the gas. The concentrations of thiocyanate and thiosulfate would be low in liquors produced in such plants.

Little is known about the cyanide content of the gas. It depends to some extent on the system and temperature of carbonization. If the cyanide is removed from the gas in a cyanide washer in which it is usually converted into thiocyanate, subsequent formation of thiocyanate should be greatly diminished.[329, 331]

The effect of the individual factors on the thiocyanate and thiosulfate concentrations in the liquor cannot be gauged, but the total effect is shown by the range in concentrations of thiocyanate, which has varied from 0.5 gram per liter under the best conditions to 15 grams per liter under the worst, according to Key.[329]

Pickles[332] reported that the production of liquors containing phenols, thiocyanates, and other compounds could be obviated by passing the gas from the retorts through a sulfuric acid bath and maintaining it in

[328] See pp. 71–2 of ref. 11. Bailey, T. L., *Gas J.*, **182**, 1016–8 (1928); **192**, 730–3 (1930); *Trans. Inst. Gas Engrs.*, **78**, 256–66 (1928–29), **80**, 201–23 (1930–31); *Inst. Gas Engrs., Commun.* **21**, 12–30 (1930); *Gas World*, **93**, 594 (1930). Key, A., and Cobb, J. W., *Gas J.*, **196**, No. 3571, Suppl., 14–6, 409 (1931); *Gas World*, **95**, 422–4. 466–9, 497 (1931). Robertson, R., and Calvert, H. T., *Dept. Sci. Ind. Research (Brit.), Water Pollution Research, Ann. Rept., 1931*, 37 pp.

[329] See pp. 72–3 of ref. 11. Key, A., Etheridge, W., and Eastwood, A. H., *Inst. Gas Engrs., Commun.* **77** (1933), 66 pp.; *Trans. Inst. Gas Engrs.*, **83** (1933–34); *Gas J.*, **204**, No. 3676, Suppl., 4–5, 506–10, 882–3 (1933); *Gas World*, **99**, 425–7, 466–95 (1933).

[330] Bailey, T. L., *Ann. Repts. Alkali, &c., Works*, **61**, 15–6 (1925); *Chemistry & Industry*, **44**, 835–45 (1925); *Gas J.*, **182**, 1016–8 (1928).

[331] Parker, A., *Gas J.*, **179**, 173–5 (1927).

[332] Pickles, L. S., *Gas World*, **91**, 840–5 (1929).

an acid atmosphere until it leaves the condensers The sulfuric acid does not attack the iron apparatus, owing to the protective action of a film of tar Cyanides and sulfur compounds can be washed from the gas in an alkali washer.

PURIFICATION OF AMMONIACAL LIQUORS AFTER PRODUCTION

Phenol and its homologs are the most objectionable compounds in ammoniacal liquors from coke plants, and, with the exception of ammonia, they are the only compounds which have been recovered to any extent on a commercial scale The proportion of gas liquor which is being dephenolized is increasing According to Wiegmann,[333] prior to World War II, 40 percent of the phenols in German liquors were recovered.

Processes for dephenolization are of three types, depending on whether the agent used for the extraction is a solid, a liquid, or a gas The solid agents include active carbon and bone blacks A large number of solvents have been proposed, of which benzene and crude light oil have been most widely used, but tricresyl phosphate and tar oils have also been employed The gases for extraction are steam, flue gas, and hot air In the United States, the benzene extraction process and the Koppers vapor recirculation process have proved commercially successful, and each is in use in a number of plants

SOLVENT EXTRACTION OF PHENOL

A solvent for the extraction of phenol from ammoniacal liquor should (1) be a good solvent for phenol, (2) be almost insoluble in the liquor, (3) be cheap so that losses may be replaced at small cost,[334] (4)

have a minimum tendency to emulsify with the liquor, (5) not decompose on treatment with sodium hydroxide, or when distilled, in case the phenols are separated by this means, and (6) preferably have a low vapor pressure [335] Also its density should differ sufficiently from that of liquor to permit its separation by gravity, and phenols should be easily recovered from it

Benzene Benzene satisfactorily fills these requirements, and light oil or its fractions are the only solvents used for extraction in American practice, so far as is known A typical arrangement of plant is shown in Fig 10 It consists of two series of extraction vessels, one for the removal of phenols from the liquor, the other for the recovery of phenols from the solvent For solvent extraction of the liquor, two towers are used, through which liquor and benzol are continuously passed in countercurrent flow The liquor is pumped in at the top of the first tower, the benzol at the bottom of the second The heights of the towers and of adjustable seals are so arranged that the two liquids flow uniformly in opposition to each other without further pumping Distributors for insuring intimate contact of solvent and liquor are usually installed in the towers They consist of layers of coke, spiral tile, or wooden hurdles

The phenol is removed from the benzol by washing with two successive batches of caustic soda The caustic solution, usually 20 to 30 percent sodium hydroxide, is charged periodically into each of the vessels, but the benzol solution flows continuously through the two containers in series until the caustic in the first is converted to sodium phenolate The spent solution is then replaced with fresh caustic, and the position of the washers is interchanged In

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[333] Wiegmann, H, *Gluckauf*, **75**, 965–71 (1939)

[334] See p 74 of ref 11

[335] Shaw, J A, private communication, 1941

this way, the freshest caustic is always used for the final washing of the benzol solution In a plant at Fairmont, W Va,[336] the caustic consumption was approximately 15 percent in excess of that theoretically required for formation of sodium phenolate

The efficiency of phenol removal is affected by the solvent used, the solvent: liquor ratio, the temperature of extraction, and the intimacy of contact in the extractors The solvent used in the caustic recovery process is usually crude light oil or
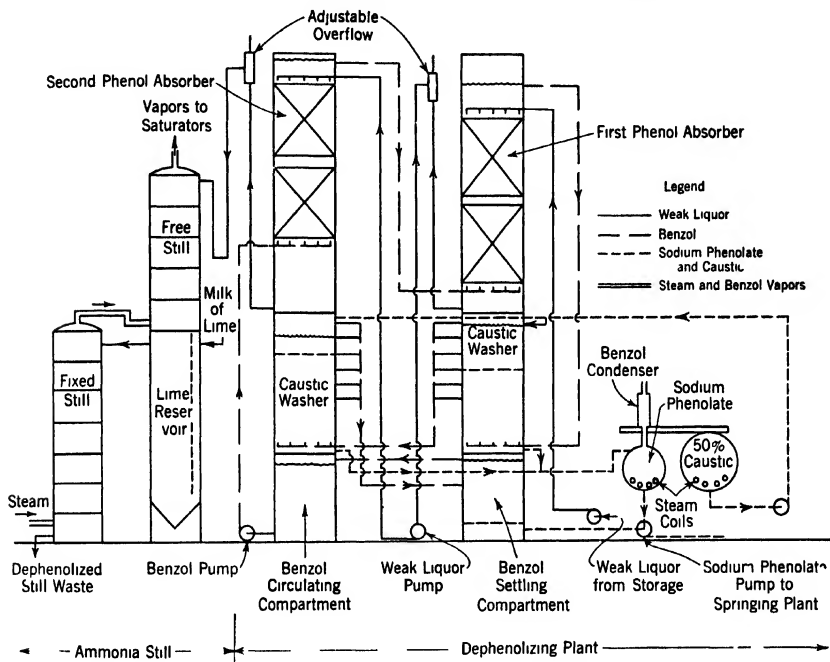
FIG 10   Flow diagram for a dephenolization plant using benzol extraction

In some European plants, the phenol and benzol have been separated by distillation The lower-boiling benzol was distilled off, and the phenol remained in the still, but Hoening[337] found that caustic scrubbing was preferable by reason of the lower cost for recovery and the higher quality of the tar acids produced

motor benzol Differences have been observed in the extraction efficiencies of these solvents At the coke plant in Troy, N Y, crude light oil gave 3 to 5 percent better dephenolization than did motor benzol[338] Wiegmann[339] recommended that a benzol suited to the liquor used be employed

In a plant in which the benzol is sepa-

[336] Jones H E, *Chem & Met Eng*, **35**, 215–8 (1928)

[337] Hoening, P, *Z angew Chem* **42**, 325–31 (1929).

[338] Williams R D, *Proc Am Gas Assoc*, 1929, 937–40.

[339] Wiegmann, H, *Gluckauf*, **64**, 397–404, 435–41, 605–6 (1928)

rated from the phenol by distillation, use of a refined benzol fraction will avoid contamination of the tar acids with the higher-boiling compounds of the light oil. Hoening [337] recommended benzol with a distillation range of 85 to 120° C.

Increase in the ratio of solvent to liquor increases the efficiency of dephenolization. The influence has been illustrated by Hoening [337] with the data reproduced in Table XXXV. When the volume of benzol is 90

TABLE XXXV

EFFECT OF BENZOL: LIQUOR RATIO ON EFFICIENCY OF DEPHENOLIZATION [337]

Benzol percent of liquor volume	Dephenolization percent
25	57
30	62
35	66
45	74
50	78

percent of the volume of liquor, 90 percent dephenolization may be expected.[340] In the United States, still higher solvent: liquor ratios are commonly employed. Dephenolization efficiencies of 95 up to 99 percent have been recorded in plants in which 1 to 1.2 volumes of solvent per volume of liquor have been circulated.[336, 341] In the distillation plants, a volume of benzol much smaller than that of the liquor has been used in order to reduce the steam consumed in distillation.

340 Holton, A. L., *Gas Engr.*, **48**, 382–5 (1931) ; *Gas J.*, **194**, 790–801, 834 (1931), **196**, 423 (1931), **200**, 687 (1932), **204**, No. 3676, Suppl., 4–5 ; 506–10, 882–3 (1933) ; *Gas World*, **94**, 625, 735 (1931), **95**, 468 (1931), **99**, 425–7, 466–95 (1933) ; *Inst. Gas Engrs., Commun.* **77**, 55–8 (1933).

341 Crawford, R. M., *Ind. Eng. Chem.*, **18**, 313–5 (1926) ; *Blast Furnace & Steel Plant*, **14**, 112–4, 154 (1926) ; *Proc. 2nd Intern. Conf. Bituminous Coal*, **2**, 726–34 (1928). Hatch, B. F., *Blast Furnace & Steel Plant*, **17**, 1797–800 (1929).

The improvement in dephenolization efficiency with increase in temperature has been shown by Hoening; [337] his data are reproduced in Table XXXVI. The higher

TABLE XXXVI

EFFECT OF TEMPERATURE ON THE EFFICIENCY OF DEPHENOLIZATION [337]

Temperature in Washer °C	Dephenolization percent
20	58
35	66
50	72
65	73

temperatures increase the loss of benzol by evaporation and the fire hazard from the inflammable solvent. Caustic recovery plants have usually been operated at ordinary temperatures. At Troy, N. Y.,[338] the temperatures were always below 100° F. In distillation plants, the temperatures have been higher. One plant used benzol equivalent to 30 percent of the volume of the liquor at 62 to 65° C and removed 75 percent of the phenol.[337] Krebs [342] recommended a temperature of 60° C for washing.

Better distribution of solvent and liquor improves the contact and increases the percentage of phenol removed. Hoening [337] supplied the following data: no packing in extractors, 55 percent dephenolization; coke packing, 60 percent; 60-millimeter Raschig rings, 70 percent; 25-millimeter Raschig rings, 73 percent; and sieve plates, 73 percent. Centrifugal pumps [343] and paddle mixers [344] have also been used for ensuring contact of liquor and solvent. The effi-

342 Krebs, O., *Chem.-Ztg.*, **57**, 721–3, 743–4 (1933).

343 Anon., *Gas World*, **85**, Coking Sect., 82–4 (1926).

344 Franke, P., *Gas- u. Wasserfach*, **68**, 244–5 (1925) ; *Chem.-Ztg.*, **49**, 825 (1925).

ciency of dephenolization is increased by increasing the height of the washer.[345]

The phenols are recovered from the sodium phenolate by "springing" with an acid, a gas containing carbon dioxide, or an acid salt, such as sodium bicarbonate:

$$NaOC_6H_5 + CO_2 + H_2O$$
$$\rightarrow C_6H_5OH + NaHCO_3$$
$$NaOC_6H_5 + NaHCO_3$$
$$\rightarrow C_6H_5OH + Na_2CO_3$$
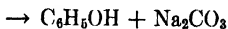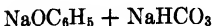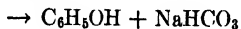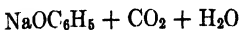
The phenol separates as a brown oil on top of the solution of sodium salts.

When sulfuric acid is used, the cost of the acid is a direct charge against the process, and the solution of sodium sulfate must be disposed of. A considerable amount of the phenols remains in the aqueous sulfate layer, the proportion depending largely on the volume, the concentration of sodium sulfate, and the temperature. Dawson [346] recovered phenols from the sulfate solution by extraction with solvents. His experiments indicated that cresylic acid of relatively high boiling point could be used advantageously for this purpose.

The carbon dioxide in boiler stack gas, the products of combustion of blast-furnace gas (22 to 24 percent carbon dioxide), or those obtained by burning coke are suitable for springing. The gas is bubbled for several hours [347] through a vertical tank containing the sodium phenolate. The solution of sodium carbonate and bicarbonate which is produced has been used in other plant processes, the Seaboard gas purification process, for instance.[347] At Troy, N. Y., by using this solution, which contained

traces of phenols, the efficiency of hydrogen sulfide removal was increased as much as 5 to 10 percent.[341] The sodium carbonate has also been causticized and the caustic solution returned to the phenol process.[348]

A sodium carbonate solution results when sodium phenolate is sprung with sodium bicarbonate. The bicarbonate has been added as a 50 percent slurry and the final solution diluted with water to prevent crystallization of salts.[388]

Crawford [349] suggested washing the benzol with a solution of sodium sulfide to extract the phenol:

$$Na_2S + C_6H_5OH \rightarrow NaHS + NaOC_6H_5$$
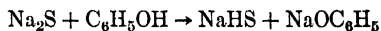
Hydrogen sulfide was passed into the sodium phenolate solution in order to "spring" the phenols. The solution of sodium bisulfide thereby produced was separated and then boiled to regenerate hydrogen sulfide and sodium sulfide, both of which were returned to the process.

Ammonium acetate-containing waters from the carbonization of peat were used by Rakovskii and Edel'shtein [350] for the decomposition of sodium phenolate. Ammonia and sodium acetate were recovered.

The phenol recovered by Crawford [341] was a reddish brown liquid with a specific gravity of about 1.05. On a dry basis, it consisted of phenol, 57 percent; o-cresol, 13 percent; m-cresol, 8 percent; p-cresol, 10 percent; and higher tar acids and residue, 12 percent. The water content varied from 2 to 12 percent. At Fairmont, W. Va., Jones [336] recovered tar acids of the following composition: phenol, 54 percent;

345 Key, A., and Cobb, J. W., *Gas J.*, **196**, No. 3571, Suppl., 14–6, 409 (1931); *Gas World*, **95**, 422–4, 466–9, 497 (1931).

346 Dawson, H. M., *J. Soc. Chem. Ind.*, **39**, 151-2T (1920).

347 See p. 655 of ref. 2.

348 Private communication, 1931.

349 Crawford, R. .M., *Ind. Eng. Chem.*, **19**, 168–9 (1927); *Blast Furnace & Steel Plant*, **14**, 400–1 (1926).

350 Rakovskii, V. E., and Edel'shtein, N. G., Russ. Pat. 46,575 (1936); *Chem. Abs.*, **33**, 3568 (1939).

cresols, 23 percent; water, 16 percent; and tarry matter, 7 percent.

Analyses of the tar acids from three German plants are shown in Table XXXVII.[339, 343] The tarry matter in these

TABLE XXXVII

ANALYSES OF TAR ACIDS FROM GERMAN PLANTS

Plant	A	B [339]
	percent	percent
Phenols	85	75 ·
Benzene	6	15
Pyridine bases	4	4
Tar	5	6

Plant	C [343]
	percent
Phenols, clean	55.0
pitch	9.3 64.3
Bases	8.8
Neutral oils	21.9
Water	1.0
Other polymerized products	4.0

analyses also originated in the liquor and was extracted by the solvents. It included pyridine bases, neutral oils, and other organic compounds.

In a semi-scale washer, Key and Cobb[345] found that 45 percent of the sulfide in the liquor was also removed by the benzene.

Phenol is the most soluble in water of the tar acids, hence extraction with an organic solvent will preferentially remove cresols and xylenols, while the phenol will tend to remain in the liquor. Analyses of the phenols in an ammoniacal liquor and in the benzol for 75 and 90 percent dephenolization conditions, respectively, have been made by Hoening,[337] Table XXXVIII.

The preferential extraction is illustrated further by an analysis of the phenols present in a liquor before and after dephenolization, Table XXXIX.[337]

Nitrogen and sulfur compounds have been eliminated from tar acids by treating

TABLE XXXVIII

ANALYSES SHOWING PREFERENTIAL EXTRACTION OF HIGHER TAR ACIDS FROM A LIQUOR [337]

Tar Acids in	Original Liquor	Benzol after Dephenolization of Liquor by	
		75 percent	90 percent
	percent	percent	percent
Phenol	36.91	20.61	30.99
o-Cresol	23.30	39.24	24.36
m-Cresol	12.74	8.51	11.77
p-Cresol	17.03	16.57	17.67
Higher phenols	10.03	11.38	10.14
Phenol pitch	.....	3.69	5.07

TABLE XXXIX

ANALYSIS OF THE TAR ACIDS IN A LIQUOR BEFORE AND AFTER DEPHENOLIZATION [337]

Tar Acids in	Original Liquor	Dephenolized Liquor
	grams per liter	
Phenol content of liquor	3.22	0.82
	percent	
Phenol	33.63	75.71
o-Cresol	21.80	15.00
m-Cresol	9.21 ⎤	
p-Cresol	21.14 ⎬	9.29
Higher phenols	15.22 ⎦	

them with sulfuric acid and distilling under vacuum. In one case,[351] 80 percent of the phenols which were purified by this treatment were recovered. They contained less than 0.05 percent nitrogen and sulfur.

The quality of the tar acids has been improved by purifying the benzol before the caustic extraction. Impurities, such as hydrogen sulfide, were removed by washing the solvent with water.[352] The solvent has also been allowed to stand until the hydrogen sulfide was oxidized, and the oxidation was accelerated by light or by

351 I. G. Farbenindustrie A.-G., Fr. Pat. 48,444 (1937), Addn. to Fr. Pat. 732,698 ; *Chem. Zentr.*, **109**, I, 4515 (1938).

352 Wingert, W. B., U. S. Pat. 1,927,883 (1933).

means of catalysts.[353] A gas, such as coke-oven gas, or another solvent, has been used to purify the benzol in a cyclical operation: first, removal of the hydrogen sulfide from the benzol by the gas, then elimination of the hydrogen sulfide from the gas.[354] The enriched benzol has been washed with acid, in order to remove pyridine bases.[342]

When the solvent is washed with caustic, much of the tarry matter absorbed from the liquor remains in the solvent and gradually accumulates. Excessive accumulations of tar in the solvent have been the cause of emulsion troubles.[355]

Solid particles of tar in the solvent have been removed by thorough settling of the liquor or by filtration. At Manchester, a tower filled with coke and steel turnings removed 1 gallon of tar per 1,000 gallons of liquor.[340] Filtration through other solid adsorbents, such as alumina, limestone, sawdust, or charcoal,[356] crushed flint, coke, or wool,[357] has been described. Tar oils which would dissolve in the solvent have been removed from the liquor by a preliminary wash with a small amount of benzol.[358] When sufficient tar accumulated in this benzol, it was distilled.[355] Johnson[359] adsorbed soluble tars from liquor by passing it through activated carbon after a preliminary filtration to remove entrained solid particles.

Emulsion gradually accumulates in the extraction vessels and benzol storage tanks. At both Troy, N. Y.,[338] and Fairmont, W.

Va.,[336] the layers of emulsion were pumped off periodically and worked up, or discharged into the gas mains before the primary cooler. Light oil was also withdrawn from circulation periodically and replaced with fresh material. Wiegmann and Röhl[360] removed from circulation and distilled a small volume of the benzol at regular intervals. The proportion removed was regulated to prevent excessive accumulation of impurities. The distillate was returned to the dephenolizing system.

Benzol is lost from a dephenolizing system by solution or entrainment in the liquor and sodium phenolate, and by evaporation. The loss in the liquor at Fairmont, W. Va., amounted to 0.14 percent by volume of the liquor at 40° C and 0.16 percent at 23° C.[315] In a plant in which the semi-direct sulfate process is used, this benzol is presumably vaporized in the ammonia still and returned to the gas. The true loss is merely the cost for recovering and processing in the benzol plant.

The residual benzol has been recovered from dephenolized liquor by passing air, steam, or both under pressure through it.[361] In other processes, it has been adsorbed by means of activated carbon[340] or washed out by means of another solvent.[362] Hoening[337] has stated that extraction of the liquor with a lignite tar oil reduced the benzol content to 0.5 gram per liter. Filtration through activated carbon reduced the benzol content of the liquor to 0.1 in one test,[363] and 0.25 gram per liter in another.[340] The benzol was recovered by steaming the carbon.

[353] Gewerkschaft Mathias Stinnes, Ger. Pat. 509,154 (1929).
[354] Gewerkschaft Mathias Stinnes, Ger. Pat. 517,001 (1929).
[355] Wiegmann, H., *Glückauf*, **68**, 33–40 (1932).
[356] Weindl, A., U. S. Pat. 1,571,986 (1926).
[357] Gutehoffnungshütte Oberhausen A.-G., Brit. Pat. 318,173 (1928); Ger. Pat. 544,664 (1928).
[358] Koppers, H., Ger. Pat. 576,427 (1933).
[359] Johnson, G. W., and I. G. Farbenindustrie A.-G., Brit. Pat. 479,359 (1938).

[360] Wiegmann, H., and Röhl, O., Ger. Pat. 551,-338 (1929).
[361] Klär- u. Entphenolungs G.m.b.H., Fr. Pat. 689,319 (1929); Brit. Pat., 341,302 (1929).
[362] Koch, E., *Teer u. Bitumen*, **26**, 281–4 (1928). Koppers, H., Ger. Pat. 567,895 (1928).
[363] Müller, C., *Petroleum*, **28**, 1 (1932).

Loss of benzol by evaporation has been reduced by venting all apparatus into a common header provided with a seal.[336, 338] At one plant, the evaporation loss was reduced by washing all the vapors from the apparatus with ammoniacal liquor in a tower packed with Raschig rings.[364] Benzol occluded in the sodium phenolate solution has been removed by boiling the solution prior to springing. The vapors were condensed and returned to the system.[336]

Dephenolization of still waste with benzol is possible if the calcium phenolate is decomposed by acidification before extraction. The process is said to be uneconomical.[365] Waste sulfuric acid and acid resins from the benzol refining process have been used for acidification.[344, 366]

Information on the dephenolizing plants in the Ohio Valley and operating results have been given by Waring.[367] The experience with the benzol process in the Ruhr in Germany has been described by Wiegmann.[339, 355, 368] Alkali extraction for recovery of the phenol proved cheaper than distillation and gave a better yield.[337, 369] The phenol removal plants in the Ruhr did not reduce the phenol concentration sufficiently to protect the water supplies, and Wiegmann[368] recommended that they be followed by biological purifi-

cation plants to remove the last traces of phenol.

Data on the distribution of phenol between benzol and water, although available in the literature,[370] should not be applied directly to the mixtures encountered in actual practice. The data are chiefly of value for comparisons between solvents.

Methods for increasing the solubility of the phenol in the benzene fraction, both the addition of other solvents and the use of other coal-tar fractions, have been investigated. It is probable that none of the other solvents which have been proposed have been used more than to a limited extent. The addition of organic bases, such as aniline, quinoline, or pyridine, to the benzol has improved the efficiency of the phenol extraction.[371] Ulrich[372] has added the bases to the liquor itself before treatment with the solvent. Kazachkov[373] reported that 1 part of a 30 percent solution of heavy pyridine bases in xylene removed 96 to 99 percent of the phenols from 5 parts of liquor containing 4 grams per liter of phenols.

Distribution coefficients for phenol and *m*-cresol between water and various solvents have been given by von Walther and Lachmann,[370] Table XL. Quinoline remaining in the water after treatment with the benzol-quinoline mixture amounted to 2.09 grams per liter; and 13.64 grams per

364 Key, A., and Etheridge, W., *Inst. Gas Engrs., Commun.* **77**, (1933), 66 pp.; *Gas J.*, **204**, No. 3676, Suppl., 4–5, 506–10, 882–3 (1933); *Gas World*, **99**, 425–7, 466–95 (1933).

365 Raschig, F., *Z. angew. Chem*, **40**, 897–8 (1927). Weindl, A., *Gluckauf*, **63**, 401–9 (1927).

366 Posseyer, E., and Abwasser u. Wasserreinigungs G.m.b.H., Brit. Pat. 175,285 (1922). Ger. Pat 431,244 (1922).

367 Waring, F. H., *Am. J. Pub. Health*, **19**, 758–70, 817–22, 929–34 (1929).

368 Wiegmann, H., *Gas- u. Wasserfach*, **75**, 433–6 (1932).

369 Weindl, A., *Gluckauf*, **64**, 498–502 (1928). Monkhouse, A. C., *Gas J.*, **188**, Suppl., 55–64, 66–70 (1929).

370 Rothmund, V., and Wilsmore, N. T. M., *Z. physik. Chem.*, **40**, 611–28 (1902). Philip, J. C., and Bramley, A., *J. Chem. Soc*, **107**, 377–87 (1915). Von Walther, R., and Lachmann, K., *Braunkohlenarch.*, **31**, 29–43 (1930); *Brennstoff-Chem.*, **12**, 113 (1931). Schumann, L., *Chem. Obzor*, **9**, 23–7, in English 27 (1934); *Chem. Abs*, **28**, 4856 (1934).

371 Stinnes, Z. M., Brit. Pat. 249,111 (1925). Anon., *Chimie et industrie*, **22**, 419–20 (1929).

372 Ulrich, F., U. S. Pat. 1,795,382 (1931).

373 Kazachkov, L. I., *J. Chem. Ind.* (*U.S.S.R.*), **8**, 720–3 (1931); *Chem. Abs.*, **26**, 1754 (1932); *Ind. Eng. Chem., News Ed.*, **11**, 284 (1933).

TABLE XL

DISTRIBUTION COEFFICIENTS FOR PHENOL AND
m-CRESOL BETWEEN THE SOLVENT AND
WATER [370]

Solvent	Phenol	m-Cresol
90 percent benzol	2.3	7 2
80 percent benzol, 20 percent quinoline	81.0	238.5
75 percent benzol, 25 percent aniline	4.5	......
Solvent naphtha from lignite distillation	0.09	0.54
Yellow oil from lignite distillation	0.32	1.20

liter of aniline remained after the benzol-aniline extraction.[370]

The addition of tar bases to benzol increased its extraction efficiency for higher tar acids. With a 4 : 1 mixture of benzol and aniline oil, a 50 percent removal of such tar acids as catechol was obtained, as compared to 8 percent with benzol alone.[374]

Key and coworkers [375] found that the distribution coefficients for phenols between tar oils and water were higher than between benzol and water; but, if the bases were removed from the tar oils, the coefficients were the same. The recovered phenols could be distilled from the solvent if the solvent boiled above 200° C.

The use of a solvent consisting of benzol plus a high-boiling fraction of the benzol still residue has been proposed.[376] Tar and high-boiling tar fractions have also been patented as solvents.[377] One German plant was operated with a tar oil distilling between 230 and 270° C.[369] The fractions may contain their original concentration of

tar acids.[378] The use of tar acids boiling from 230 to 350° C has also been recommended.[379]

In laboratory experiments, Crawford [380] found that a light tar oil (sp. gr. 0.953 at 30° C, tar acid content 0.6 percent) would remove 93 percent of the phenols from an equal volume of liquor, whereas the same proportion of motor benzol removed only 73 percent. Kazachkov [378] found that 60 parts of anthracene oil removed 77 percent of the phenol from 100 parts of a phenolic effluent.

Benzol, benzine, trichloroethylene, and their mixtures have been introduced into the extractor as vapors The liquor was sprayed in, the vapor condensed, and the solvent-liquor mixture separated.[344, 381] Trichloroethylene has advantages, in that it is noninflammable and is less soluble in the liquor than benzol.[344] Numerous patents have been issued on the benzol dephenolization process, in addition to those cited.[382] Methods for incorporating benzol dephenolizing plants in coking operations have been diagrammed by Wiegmann.[383]

Tricresyl Phosphate. The use of triaryl, trialkyl, and triaralkyl phosphates as solvents for the dephenolization of ammoni-

[374] Monkhouse, A. C., and Etheridge, W , *Inst. Gas Engrs., Commun.* 21, 12–30 (1930). Botley, C. F., et al., *Trans. Inst. Gas Engrs.,* 80, 187–233 (1930–31) ; *Gas J.,* 192, 730–3 (1930) ; *Gas World,* 93, 594 (1930).

[375] Key, A., Etheridge, W., and Eastwood, A. H., *Trans. Inst. Gas Engrs.,* 82, 397–462 (1932–3) ; *Inst. Gas Engrs., Commun.* 60, (1932), 50 pp.

[376] Otto, C., and Co., G.m.b.H., Ger. Pats. 553,410, 555,157 (1928).

[377] Miller, S. P., U. S. Pats. 1,873,900–1 (1932), 2,045,607–8 (1936). Ulrich, F., U. S. Pat. 1,830,725 (1931).

[378] Braun, C. E., Can. Pat. 318,640 (1932) ; U. S. Pat. 1,937,941 (1933).

[379] Molinari, V., U. S. Pat. 2,073,248 (1937). Weindl, A., Brit. Pat. 279,465 (1926).

[380] Crawford, R. M., *Ind. Eng. Chem.,* 19, 966–8 (1927).

[381] Posseyer-Meguin A.-G., Ger. Pat. 481,738 (1922). Klär- u. Entphenolungs. G.m.b.H., Fr. Pat. 683,793 (1929). Otto, C., and Co., G.m.b.H., Ger. Pat. 590,476 (1934).

[382] Raschig, F., Brit. Pat. 287,226 (1926) ; Fr. Pat. 636,301 (1927). Wiegmann, M., and Röhl, O., Ger. Pat. 550,255 (1928). Humphreys and Glasgow, Ltd., Fr. Pat. 684,796 (1929). Kuneberger, A. F., Brit. Pat. 348,100 (1929). Cobb, H. B., U. S. Pat. 1,943,653 (1934). Koppers Co., Brit. Pat. 400,162 (1934). Tiddy, W., U. S. Pat. 1,989,177 (1935).

[383] Wiegmann, H., *Brennstoff-Chem.,* 11, 285–8, 304–6 (1930).

acal liquors also has been patented,[384] and tricresyl phosphate has been used in several German plants, particularly in those for brown-coal distillation and hydrogenation.[385] Tricresyl phosphate is a neutral liquid which has a specific gravity of 1.18 at 20° C and boils about 280–285° C under 10-millimeter pressure.[386]

Comparisons of benzol and tricresyl phosphate for extraction of phenol[386, 387] show that the processes differ in the following respects:

1. The absorbing capacity of the phosphate is much higher than that of benzol. The partition coefficients of phenols between each of the two solvents and water have been compared by Schönburg[386] in a graph, values from which are shown in Table XLI. In German plants, the volume

TABLE XLI

Partition Coefficients for Phenols Between Tricresyl Phosphate and Water, and Benzol and Water [386]

Tar Acid	Partition Coefficient with		Ratio of Partition Coefficients
	Tricresyl Phosphate	Benzol	
Phenol	60	1.9	31
o-Cresol	210	13.0	16
p-Cresol	196	11.5	17
Phenol mixture in waste liquor	88	5.2	17

of the phosphate used was 8 to 10 percent of the volume of liquors which contained 3 to 5 grams per liter of phenols, when

384 Schönburg, C., and von der Bruck, G., Brit. Pat. 328,388 (1929) ; Fr. Pat. 687,275 (1929) ; Ger. Pat. 532,291 (1929) ; U. S. Pat. 1,826,369 (1931). Deiters, W., Herold, P., Koppe, P., and Lüttge, F., U. S. Pat. 2,086,856 (1937).

385 Gösmeier-Kres, E., Brennstoff-Chem., 17, 466–70 (1936).

386 Schönburg, C., Brennstoff-Chem., 12, 69–71 (1931) ; Gas J., 193, 643 (1931) ; Chem. Trade J., 88, 274 (1931).

387 Tupholme, C. H. S., Ind. Eng. Chem., 25, 803–4 (1933). Lorenzen, G., Gas- u. Wasserfach, 80, 925–8 (1937).

extracted at 20–30° C. Shorter extraction towers can therefore be used with the phosphate than with benzol.[387]

2. Because the specific gravity of the phosphate is greater than that of the liquor, the directions of flow of the solvent and liquor are the reverse of those with benzol.

3. Recovery of phenols from tricresyl phosphate is best accomplished by distillation under vacuum (absolute pressure about 35 millimeters of mercury).[385] By distillation under atmospheric pressure, only 77 percent of the phenols were removed, and decomposition of the solvent and the tarry matter, also extracted from the liquor, darkened the solvent and increased its viscosity. Extraction with caustic was not satisfactory, owing to the formation of emulsions.[387]

4. The quality of the tar acids from tricresyl phosphate is said to be higher than from benzol, because the acids are separated from the benzol by distillation.[387] However they should be redissolved in caustic soda in order to separate neutral oils before being used for the production of pure phenol.[388] Although Schönburg[386] reported that tricresyl phosphate has a selective action and absorbs less tarry matter than benzol, Lorenzen[387] recommended that the liquor be freed from tar, oils, and solids, before extraction, and that the hydrogen sulfide content should be low. The I. G. Farbenindustrie patented methods for keeping oily and tarry matter out of the tricresyl phosphate by passing both liquor and solvent through activated carbon.[389] Mond[390] removed pyridine bases and tar oils by extracting the phenols from the solvent with an alkali and steaming the alkali solution before springing.

388 Shaw, J. A., private communication, 1941.

389 I. G. Farbenindustrie A.-G., Fr. Pat. 823,-623 (1938) ; Belg. Pat. 422,310 (1937).

390 Mond, A. L., Brit. Pat. 328,388 (1930).

5. The loss of tricresyl phosphate in the liquor has been reported by Gösmeier-Kres [385] to be only 0.050 to 0.080 gram per liter. Although this is less than the loss of benzol, when reckoned on the value of the solvent, there may be little difference in cost.[387] The loss in the liquor was somewhat greater than the solubility of tricresyl phosphate in water, which is 0.030 gram per liter.[385]

6. Tricresyl phosphate deteriorates with use and must be purified or renewed at intervals.[385, 387, 389] A portion of the solvent is withdrawn periodically and treated with concentrated sulfuric acid, while being heated with steam. The mixture is neutralized with lime and centrifuged to remove the sludge.[385]

7. The initial cost of tricresyl phosphate is much greater than that of benzol.

8. Tricresyl phosphate is less volatile and less inflammable than benzol.

Gösmeier-Kres [385] has supplied data on the material requirements in a German plant, treating from 120,000 to 250,000 gallons of liquor per day: steam, 200 to 350 pounds per 1,000 gallons of liquor; electric power, 4 kilowatt-hours per 1,000 gallons of liquor; cooling water, 3,000 gallons per 1,000 gallons of liquor; tricresyl phosphate, 100 to 220 pounds per day; and labor, 72 man-hours (3-shift operation).

Tritolyl phosphate is similar to tricresyl phosphate in its high absorbing capacity and small losses. Because of its high density, Agafoshin [391] recommended that the extraction should be performed in steps. Extractions should be carried out at ordinary temperatures, because at higher temperatures the extracting power of the phosphate is reduced. The tritolyl phosphate concentration in the dephenolized liquor

(0.069 gram per liter) did not interfere with the biological purification of the liquor.

The I. G. Farbenindustrie [392] has patented the extraction of ammoniacal liquors with organic phosphates in the presence of inert gases, such as waste combustion gases. The gases facilitated the separation of the emulsion-forming substances as a foam on top of the liquor. Foam-forming substances could be added to the solvent-liquor mixture in order to facilitate this separation.

A process combining dephenolization with tricresyl phosphate followed by bacterial purification, has also been patented by the I. G. Farbenindustrie.[393]

Other Solvents. Other solvents used for the extraction of phenols include petroleum oils, such as benzol wash oil [394] and kerosene; [395] hydrogenated oils, including those produced from tar oils or the acid oils obtained in benzol refining; [396] mixtures of alcohols, insoluble in water, with boiling points ranging from 130 to 210° C, which are obtained by hydrogenation of carbon monoxide; [397] diaryl ethers, preferably $(C_6H_5)_2O$, either alone or in solution with other solvents; [398] esters of carboxylic acids, such as ethyl or butyl acetate; [399] and trichloroethylene.[400] The

391 Agafoshin, N. P., *Vodosnabzhenie i Sanit. Tekh.*, 3, No. 4, 68–73, No. 5, 82–9 (1938) ; *Chem. Abs.*, 33, 9506 (1939).

392 I. G. Farbenindustrie A.-G., Brit. Pat. 450,-716 (1936).

393 I. G. Farbenindustrie A.-G., Brit. Pat. 502,-193 (1939).

394 Wingert, W. B., U. S. Pat. 1,963,516 (1934).

395 Shaw, J. A., U. S. Pat. 1,832,140 (1931).

396 Potts, H. E., et al., Brit. Pat. 450,789 (1936).

397 Burdick, C. L., U. S. Pat. 1,986,820 (1935).

398 Chemische Fabrik von Heyden A.-G., Brit. Pat. 495,163 (1938) ; Fr. Pat. 832,300 (1938).

399 I. G. Farbenindustrie A.-G., Brit. Pat. 520,198 (1939).

400 Franke, P., *Gas- u. Wasserfach*, 68, 244–5 (1925).

phenol may be recovered from many of these solvents by caustic extraction in the usual way.

Bruns [401] disclosed the use of hot wash oil from the benzol still for extraction of phenols from ammoniacal liquor. The enriched solvent was cooled by direct contact with water, which also dissolved impurities absorbed from the liquor.

Kazachkov [402] made laboratory experiments on the extraction of phenol from water by paraffin oil, kerosene, benzols, sunflower oil, castor oil, fish oil, and oleic acid. Castor oil proved the best; 1 volume would extract 55 percent of the phenol from 2 volumes of a 1-gram-per-liter solution, and 87 percent from 2 volumes of a 10-gram-per-liter solution.

[401] Bruns, H., Ger. Pats. 504,337 (1926), 516,527 (1931), 567,666 (1933).

[402] Kazachkov, L. I., J. Chem. Ind. (U.S.S.R.), 8, 720–3 (1931); Chem. Abs., 26, 1754 (1932).

DEPHENOLIZATION BY VAPORIZATION OF PHENOL

Koppers Vapor Recirculation Process. Phenol has an appreciable vapor pressure, particularly at steam temperatures, and processes have been developed for removing the phenol from ammoniacal liquor by vaporization, using steam, hot air, or other gases. The process developed by the Koppers Company of Pittsburgh has been installed in a number of American coke plants.[403, 404] The principle of this process is the continuous recirculation of a current of steam, first through the hot ammonia liquor to vaporize the phenol and then through a caustic soda solution to absorb the phenol in the steam. A flow sheet for

[403] Shaw, J. A., Brit. Pat. 299,837 (1928). Hatch, B. F., Ind. Eng. Chem., 21, 431–3 (1929); Blast Furnace & Steel Plant, 17, 1493–6 (1929). Wilson, P. J., Proc. Am. Gas Assoc., 1929, 934–6.

[404] See pp. 652–5 of ref. 2.
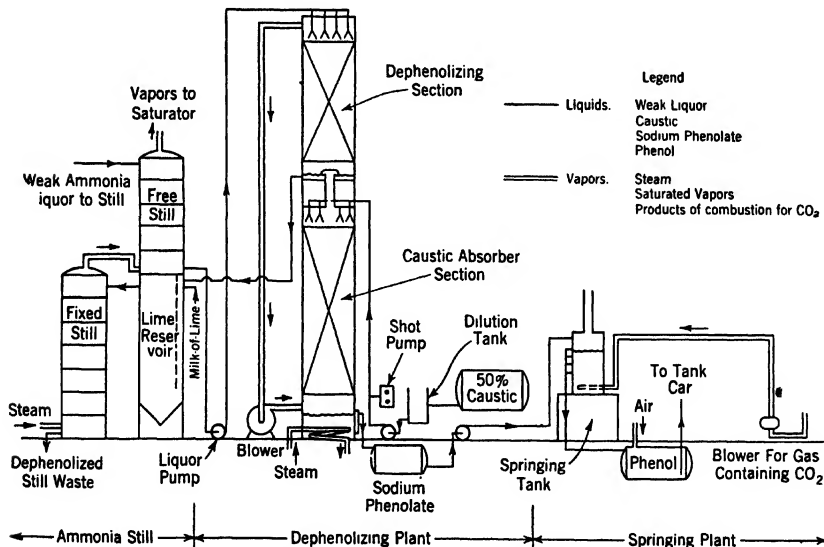
FIG. 11. Flow diagram of the Koppers vapor recirculation process for dephenolizing ammoniacal liquors.

the process is shown in Fig. 11.[405] A plant consists essentially of a tower divided into two sections, through which steam under a slight pressure and at a temperature of around 100° C is recirculated by means of a blower. The upper section of the tower is packed with wooden hurdles or spiral tile, over which the liquor is sprayed. The phenol is removed by the current of steam passing countercurrent to the liquor. The

ings, the sodium phenolate solution, which has drained from the shot section, is recirculated in order to insure removal of the phenols from the steam.[406]

The process can be readily adapted to give any degree of phenol removal that is reasonably required. Typical operating results from a plant in Philadelphia, Pa., are shown in Table XLII.[404] In calculating the total phenol removal of Table XLII,

TABLE XLII

OPERATING RESULTS IN KOPPERS PROCESS DEPHENOLIZING PLANT [404]

Test No.	1	2	3	4
Weak liquor to still, gallons per hour	2,000	1,500	1,500	2,000
Phenol in liquor to still, grams per liter	2.75	3.00	2.10	2.20
Phenol in liquor to dephenolizer, grams per liter	1.85	2.60	1.63	1.40
Phenol in liquor from dephenolizer, grams per liter	0.09	0.09	0.09	0.08
Phenol in still waste, grams per liter	0.05	0.06	0.05	0.05
Reduction in phenol concentration in free ammonia still, percent	32.7	13.3	22.4	36.4
Phenol removal in dephenolizer, percent	95.1	96.5	94.4	94.2
Total phenol removal, percent	97.4	97.0	96.6	96.8

liquor to be dephenolized is taken from the base of the free ammonia still and is therefore free from the acidic gases, carbon dioxide, hydrogen sulfide, and hydrogen cyanide. The dephenolized liquor is returned to the lime leg of the ammonia still from the base of the upper section of the tower.

The steam containing the phenol leaves the top of the tower and is returned by the blower to the bottom of the lower section. This is packed with steel lathe turnings, which are wetted by shots of a hot 10 percent caustic soda solution. The whole system is insulated, and heat losses are very small. In some towers, one or two recirculation sections have been introduced below the shot section. Through these sections, also packed with steel turn-

allowance has been made for dilution of the liquor with condensed steam and milk-of-lime in the still. The figures show a reduction in the phenol content of the liquor in the free still. This is partly due to dilution from condensed steam but also to loss of phenol in the steam from the still. In order to recover this phenol, which represents a loss to the process, Denig [407] patented the restriction of the steam and vapors entering the free still from the fixed still to that amount which was just sufficient to carry off the acidic gases, carbon dioxide, hydrogen sulfide, and hydrocyanic acid. When using this quantity of steam, substantially all the phenol remained in the liquor which passed on to the dephenolizer. The excess steam from the fixed still by-

[405] Powell, A. R., *Chem. & Met. Eng.*, **38**, 541–2 (1931).

[406] Wilson, P. J., *Proc. Am. Gas Assoc.*, **1929**, 934–6; *Gas Engr.*, **47**, 34 (1930).
[407] Denig, F., Brit. Pat. 463,217 (1937); U. S. Pat. 2,127,503 (1938).

passed the free still and went directly to the gas main.

At Hamilton, Ohio,[404] the dephenolizing plant was operated with more than 70 percent of the caustic converted to sodium phenolate; but in daily operation, from 30 to 50 percent of the total caustic to the dephenolizing tower was utilized. A higher conversion was not obtained because all the caustic required for washing the benzol in the agitator was first added to the dephenolizing tower. The sodium phenolate solution was then sent to the acid washer in the light-oil plant. The caustic thus did double duty, first in removing the benzol from the liquor, and then in the regular manner for benzol washing. The caustic converted to sodium phenolate was equally as good as the free caustic in the benzol washing operation.

The sodium phenolate from Koppers process plants has been sprung in the usual manner with gases high in carbon dioxide. Since the phenols have been removed from the liquor and transferred to the caustic as a vapor, an excellent product uncontaminated with tar and other impurities from the liquor is obtained. Results of the Koppers Company over a period of years show that these tar acids can be sent to the refining still for the production of pure phenol, without steaming the phenolate.[408]

Modifications of this process and the apparatus have been described in a number of patents.[409] Koppers[410] patented the recovery of some of the pyridine bases in the same process with the phenol. The

free ammonia was distilled from the liquor in the free still. The liquor from the base of this still was then dephenolized with recirculated steam. The pyridine vaporized at the same time was absorbed by passing the enriched steam through an acid scrubber. The phenol was finally absorbed with caustic in the usual way.

Heffner-Tiddy Dephenolization Process. The Heffner-Tiddy[411] process for the dephenolization of ammoniacal liquor was based on the formation of ammonium salts of the phenols during distillation. The inventors said that these salts are more readily volatile with steam than the phenols themselves, and are distilled off with the ammonia. They claimed that a large fraction of the phenols which are vaporized from the liquor in the still is condensed in the top ring by the cool weak liquor feed. The Heffner-Tiddy process aimed to prevent this condensation by admitting the feed at a temperature of 98° C or higher. It was admitted at the top of a short scrubber section, which formed an extension to the free ammonia still. In this scrubber, the ammonia concentration was built up by addition of ammonia ascending from the still, in order to obtain a concentration equivalent to that of the phenols. Hatch reported that[412] the hot gases left the scrubber section at approximately 110° C and entered a dephlegmator, in which they were cooled to 105° C. The gases from the dephlegmator containing the ammonia and phenols were returned to the gas main before the saturator. The process was installed at a coke plant in Midland, Pa.[412]

In the Heffner-Tiddy process no phenols

[408] Shaw, J. A., private communication, 1941.

[409] Koppers Co., Ger. Pats. 552,536 (1925), 667,628 (1938); Fr. Pat. 667,122 (1929); Brit. Pat. 380,699 (1933). Shoeld, M., Brit. Pat. 356,116 (1929). Sperr, F. W., and Shaw, J. A., U. S. Pat. 1,920,604 (1933). Bragg, G. A., Brit. Pat. 427,890 (1935); U. S. Pat. 2,056,063 (1936).

[410] Koppers, H., U. S. Pat. 1,905,108 (1933).

[411] Heffner, L. W., and Tiddy, W., Brit. Pats. 244,774–5 (1924); U. S. Pats. 1,566,795–6 (1925), 1,595,602–4 (1926). Tiddy, W., U. S. Pat. 1,878,979 (1932).

[412] Hatch, B. F., *Blast Furnace & Steel Plant,* 18, 296–8 (1930).

are recovered. Powell [413] has pointed out that, when the phenols are returned to the gas, the possibility of having them reappear at a later stage of byproduct recovery, in the final cooler water, for instance, is encountered.

The increased volatility of phenol in the presence of ammonia, which is the basis of the process, has not been borne out by the experimental data available. Thus, Key and coworkers [414] found that ammonia was 6.2 times as volatile in steam as phenol, and that the presence of the ammonia retards the distillation of phenols.

Laboratory experiments made by Bailey [415] on the volatilization of phenol from ammoniacal liquors showed that an increase in the proportion of ammonia had little, if any, effect on the rate of vaporization of phenol. The maximum amount of phenol removed was obtained in the absence of ammonia. His results are shown in Table XLIII.

TABLE XLIII

Composition of Solution Distilled		Phenol Volatilized (60 percent of solution distilled over in each case)
Phenol	NH$_3$	Percent of Total
grams per liter		
2.0	0	82
2.0	10	78
2.0	20	78
2.0	25	77
2.0	30	76
2.0	60	78

Other Processes. A process developed by Moses and Mackey [416] at Belle, W. Va., was reported to have removed 98 to 99 percent of the phenol from a liquor containing 5 grams per liter of tar acids. The plant consisted of a stripping column containing 27 plates, through which exhaust steam was passed. The steam requirement was high; it amounted to 59 percent by weight of the liquor. The vapors from the column were condensed and used for quenching coke.

Other processes involving the vaporization of phenols from ammoniacal liquors have been described, particularly in the patent literature. In 1910, Radcliffe [417] eliminated phenols and other impurities by acidifying the liquor and blowing gas through it. A similar process was described by Wagner, [418] who discussed, in another process, [419] dephenolization of liquor by use of reducing gases, such as hydrogen, carbon monoxide, or methane, in the presence of copper, platinum, or other catalysts. Finely divided iron could then be employed to remove other impurities.

Hot flue gases have been recommended by the I. G. Farbenindustrie [420] for removing phenols from waste liquor. Sulfur dioxide may be added to the gases. [421] The I. G. Farbenindustrie also distilled and rectified liquor containing phenols in a column, and the phenols which were separated from the distillate were withdrawn. If carbon dioxide was added to the gases, a solution

[413] Powell, A. R., *Proc. Am. Gas Assoc.*, **1929**, 928–33; *Gas Engr.*, **47**, 32–3, 34 (1930).

[414] Key, A., and Etheridge, W., *Inst. Gas Engrs., Commun.* **77** (1933), 66 pp.; *Trans. Inst. Gas Engrs.*, **83**, 166–71 (1933–4); *Gas J.*, **204**, No. 3676, Suppl., 4–5, 506–10, 882–8 (1933); *Gas World*, **99**, 425–7, 466–95 (1935).

[415] Bailey, T. L., *Ann. Rept. Alkali, &c., Works*, **63**, 28–9 (1927).

[416] Moses, D. V., and Mackey, B. H., *Chem. & Met. Eng.*, **39**, 441–3 (1932); *Am. Gas J.*, **137**, No. 2, 21 (1932).

[417] Radcliffe, J., Brit. Pat. 16,924 (1908).

[418] Wagner, F. W., U. S. Pat. 1,473,750 (1923).

[419] Wagner, F. W., U. S. Pat. 1,428,618 (1922).

[420] I. G. Farbenindustrie A.-G., Ger. Pat. 666,-504 (1938); Fr. Pat. 797,348 (1938).

[421] I. G. Farbenindustrie A.-G., Brit. Pat. 451,-180 (1936).

of ammonium carbonate was obtained as a byproduct.[422]

Phenol was removed from gas liquor by use of flue gases and live steam in a countercurrent tower packed with checker brick, according to Smith.[423] The efficiency of dephenolization amounted to 90 percent when 72,000 pounds of steam were used on 20,000 gallons of liquor per day. A minimum temperature of 98° C at the top of the tower was necessary.

Bailey[424] concluded that dephenolizing towers using stack gases did not efficiently remove the tar acids from liquors, and the fuel consumption was high in proportion to the work done. Solids separated on the tower packing. At one plant an open trough, located in one of the hot flues, was fitted with a steam coil and perforated pipe for the injection of flue gases under controlled conditions. The dephenolizing efficiency of this arrangement proved low.

Coxon[425] used steam plus flue gases for dephenolizing liquors, and introduced the mixture of vapors into a gas producer. Ammoniacal liquor was acidified with sulfuric acid and then concentrated and purified by contact with hot gases from furnaces.[426] Taylor[427] concentrated the liquor and, in doing so, boiled off the phenols.

Ammoniacal liquor was distilled by Krebs[428] to remove ammonia and the acid gases; the phenols were then distilled off with a hot steam-air mixture. The gases from the second stage were washed with caustic to recover the phenol.

Nevyazhskaya[429] and coworkers recovered sodium phenolates from the aqueous liquors obtained in the gasification of peat. The liquor containing 5 to 18 grams per liter of phenols was treated with lime and then with live steam. The vapors containing the phenols were passed through a bubble tower containing an alkali, preferably caustic soda. In addition to the phenolates, calcium acetate was a product of the process.

In several processes organic vapors have been employed. Knapp[430] treated ammoniacal liquor with a vaporous absorbing medium, such as benzene. The vapors containing the phenols were condensed, and the phenols and pyridine bases were washed out of the condensate with caustic and acid, respectively. The benzene was distilled.

The phenols have been recovered from the distillation-process gases by washing them with solvents, such as gasoline, benzene, paraffin, naphtha, and creosote.[431] The Standard Oil Company[432] removed phenols from steam by washing with a hydrocarbon at 110° C.

A distillation process has been patented by Gruhl,[433] which works unlike the processes just described. The phenol was rectified from the current of vapors in a condensing column and was retained in the still kettle. He claimed that the tarry liquor could be thus concentrated until the

[422] I. G. Farbenindustrie A.-G., Ger. Pats. 670,-272, 675,391 (1939); Brit. Pat. 438,124 (1935).

[423] Smith, W. P., *Gas J.*, **181**, 690–2 (1928).

[424] Bailey, T. L., *Ann. Rept. Alkali, &c., Works*, **63**, 17–21 (1927).

[425] Coxon, T., and Imperial Chemical Industries, Ltd., Brit. Pat. 372,801 (1932).

[426] Van Vollenhoven, C., Brit. Pat. 255,111 (1925).

[427] Taylor, A. M., U. S. Pat. 2,056,748 (1936).

[428] Krebs, O., *Chem.-Ztg.*, **57**, 721–3, 743–4 (1933)

[429] Nevyazhskaya, L. M., Vasilyuk, K. L., Nikolaev, P. N., Chirkov, P. P., and Federov, L. E., *Khim. Tverdogo Topliva*, **8**, 286–94 (1937); *Chem. Abs.*, **32**, 1429 (1938).

[430] Knapp, W. R., U. S. Pat. 1,878,927 (1932).

[431] Shadbolt, S. M., and Chemical Engineering and Wilton's Patent Furnace Co., Ltd., Brit. Pat. 276,393 (1926). Raschig, F., G.m.b.H., Fr. Pat. 698,390 (1930); Ger. Pat. 545,413 (1933).

[432] Standard Oil Development Co., Fr. Pat. 806,109 (1936).

[433] Gruhl, P., Brit. Pat. 345,579 (1930); Fr. Pat. 696,837 (1930).

water content of the residues amounted to only 10 percent.

Caustic soda has been added to ammoniacal liquor and still waste, in order to fix the phenols. The liquors have then been evaporated to produce concentrated sodium phenolate solutions.[434]

ACTIVATED-CARBON DEPHENOLIZATION

Activated carbon will adsorb phenols from ammoniacal liquor. A process has been patented by the Carbo-Norit-Union Verwaltungs-Gesellschaft,[435] and several installations have been made in Germany.[436] The process functions continuously and consists of four main operations: (1) removal of suspended matter from the liquor; (2) extraction of the phenol in the active carbon adsorbers; (3) extraction of the phenol from the carbon by solution in benzol; and (4) separation of benzol from phenols by distillation.

Efficient removal of the suspended tarry matter from the liquor, prior to dephenolization, is essential. Any tarry matter carried into the adsorbers will be largely deposited in the pores of the carbon and will eventually reduce the efficiency of adsorption. At the German Langendreer[436] plant, the liquor was first passed into the base of two tar absorbers in parallel. The conical bottoms of these vessels were filled with a layer of tar, above which 8 feet of steel turnings was supported between perforated plates. The liquor, after passage through the two purifying vessels, was further cleaned by filtration through a layer of coke in a third vessel. These treatments

reduced the tar content of the liquor, which entered the plant containing 0.8 to 1.5 down to 0.02 to 0.03 gram per liter.

The liquor, after removal of the tar, was preheated to 60 to 65° C and admitted to one of the three adsorbers. Each of these vessels was filled with active carbon of about 1.5- to 2-millimeter size. Passage of the liquor through the carbon was continued until the "break point" for the phenol was reached, when the liquor was switched to a fresh adsorber. Over 99 percent of the phenol was removed from the liquor, and the final phenol content was reduced to 0.05 to 0.1 gram per liter.[436] The carbon would absorb phenols up to 5 to 10 percent of its weight.[437]

The phenol was then extracted from the carbon in the first adsorber by slowly washing with benzol at a temperature of 60 to 65° C. A volume of benzol equal to approximately 8 percent of the volume of the liquor was required. The phenol content of the benzol from the adsorber averaged 1 to 1.5 percent. The benzol-phenol solution was passed through a separator to remove entrained liquor and discharged into a column still. When extraction of the carbon was completed, the benzol was drained from the adsorber and the residual benzol on the adsorbent vaporized with steam. After cooling, the adsorber was ready to dephenolize more liquor.

In the still, the benzol was distilled from the phenol, condensed, and returned to benzol storage for further use. Several analyses of the crude phenols produced have been reported by Sierp and are shown in Table XLIV.[436] The process was so arranged that one adsorber was always running on liquor, a second was being regenerated, and the third was ready for use.

[434] Bruns, H., Ger. Pats. 481,306 (1925), 510,056 (1930). Schmidt, H., Ger. Pat. 541,148 (1929).

[435] Carbo-Norit Union Verwaltungs-G.m.b.H., Ger Pats., 534,204 (1928), 540,054, 543,014–5, 545,160 (1929), 579,643, 594,949 (1932). Mackert, A., U. S. Pat. 1,866,417 (1932).

[436] Anon., *Ind. Chemist.*, **6**, 327 (1930). Sierp, F., *Gas- u. Wasserfach*, **76**, 105–9 (1933).

[437] Prüss, M., *Gas- u. Wasserfach*, **72**, 791–801 (1929); *Gas J.*, **187**, 404–7 (1929). Fitz, W., *Asphalt Teer Strassenbautech.*, **30**, 552–3 (1930).

TABLE XLIV

ANALYSES OF CRUDE PHENOLS PRODUCED BY
ACTIVE CARBON DEPHENOLIZATION [436]

	percent	percent	percent
Water	0.8	0.16	.....
Neutral oils	20.8	18.73	23.41
Benzol to 100° C	7.4	3.84	.....
Pyridine	9.0	6.06	.....
Pitch	11.4	14.2	10 26
Phenol	31.54	32.56	31.41
Cresols	33.47	32.55	32.39

Adsorption of phenols on the carbon took approximately 4 hours, benzol extractions 3.5 hours, and steaming 0.5 hour.[436]

The life of the carbon is very important to the economic success of the process. Replacements amounted to 1.5 to 2.0 percent by weight of crude phenol at the Langendreer plant. Prüss[437] stated that the carbon could be revivified by extraction with benzol at least 100 times.

Kozko[438] recommended the use of dichloroethane instead of benzol or gasoline for extraction of the phenols from the carbon.

Another dephenolization process, using activated carbon, was developed by Robinson Brothers in Great Britain.[439] They acidified the liquor with carbon dioxide until almost neutral, or with mineral acids to a pH of 6 to 7. Both treatments precipitated an organic sludge. The oxygen consumption of the liquor was appreciably reduced by removal of this sludge. Because the carbon adsorbed ammonia, which is vaporized with the phenol on steaming, mineral acids are better for acidification than carbon dioxide. The acidified liquor

was passed through a series of active carbon adsorbers. The adsorbers were cut out in turn as they became saturated with phenol. Three adsorbers, containing 50 pounds of carbon each, cared for 200 gallons of liquor per hour, one adsorber being cut out every 5 hours.

In laboratory experiments, Parkes[440] recovered the phenols by heating and steaming the carbon up to a temperature of 600° C. The carbon was finally heated to 800° C. This treatment maintained the activity of the carbon with a loss of only 1 to 2 percent.

Parkes reported that over 99 percent of the phenols were removed from the liquor by adsorption with the carbon, although only about 50 percent were actually recovered. The concentration of thiocyanate in the liquor was slightly reduced, and the oxygen absorption was lowered 80 to 85 percent. Good results were obtained in the dephenolization of a low-temperature liquor, although prior removal of dihydric phenols might be necessary in the case of other liquors, Parkes concluded. Treatment of vertical-retort liquors would be uneconomical, because the costs for distillation and carbon would be high on account of high concentrations of thiocyanate.

According to Prüss,[437] recovery of phenols from the carbon by steaming causes a rapid disintegration of the carbon. A considerable volume of aqueous condensate is produced which also requires dephenolization.

Piatti and Spreckelsen[441] reported that complete removal of cresol from activated carbon was possible only with organic solvents. Large amounts of steam would be required, but steaming did not affect the

[438] Kozko, A. I., *Vodosnabzhenie Sanit. Tekh.*, **3**, No. 11, 86–92 (1938); *Khim. Referat. Zhur.*, **2**, No. 3, 103 (1939); *Chem. Abs.*, **34**, 1105 (1940).

[439] Robinson, H. W., and Parkes, D. W., U. S. Pat. 1,653,788 (1927). Robinson Bros., *Gas J.*, **179**, 546 (1927). Parkes, D. W., *J. Soc. Chem. Ind.*, **46**, 186-93T (1927), **48**, 81-6T (1929). Patton, W. D., U. S. Pat. 1,873,629 (1932).

[440] Parkes, D. W., *J. Soc. Chem. Ind.*, **48**, 81-6T (1929).

[441] Piatti, L., and Spreckelsen, O., *Z. angew. Chem.*, **43**, 308–10 (1930).

activity of the carbon. According to the Metallgesellschaft A.-G.,[442] the carbon should be kept out of contact with air. Solvent and liquor flows were so arranged as to keep the carbon covered during the transition stages. Although active carbon removes phenols almost completely, Kazachkov[443] reported that it is easily poisoned by impurities.

Ruff and Martynova[444] recovered phenols from the liquors obtained in peat carbonization. The vapors from the stills were condensed and passed through activated carbon, which was regenerated in the usual way.

Attempts have been made to utilize charcoals made from low-cost materials. Thus, Rutovskiĭ[445] obtained good results with a peat charcoal onto which he distilled his benzol directly.

For purifying liquors, the Metallgesellschaft A.-G.[446] used coke, wood charcoal, or other granular carbonaceous material with a low original power of absorption. The adsorbent was revivified by steaming, followed by burning the impurities off with gases or steam having an oxygen content less than that of air.

The I. G. Farbenindustrie[447] removed phenols from activated carbon by treatment with liquid ammonia. The phenol was recovered from the ammoniacal extract by distilling the ammonia off under 10 to 15 atmospheres pressure.

Activated carbon has been used for the removal of residual phenol left in the liquor after dephenolization by solvent extraction.[448]

Water supplies have been treated by adsorbents such as activated carbons[449] or bleaching clays[450] for removal of traces of phenols giving rise to tastes and odors. The carbon in this work is usually added as a powder.

ADDITIONAL ADSORBENTS FOR PHENOL

Bone black has been used by Basore[451] as an adsorbent for phenols. Eight to fifteen parts of bone black removed nearly all phenols and color, together with some of the thiocyanate, from 100 parts of waste liquor. The black was revivified by reburning at a temperature of 1,100° F (630° C). The phenols could be partially recovered by condensing the vapors from the furnace, or burned by drawing them into the furnace. An occasional treatment of the black with dilute acid, preferably hydrochloric, was necessary to prevent the accumulation of lime and calcium carbonate. In a semi-commercial test covering two summers, Brown[452] found that the

[442] Metallges. A.-G., Brit. Pats. 305,657 (1929), 344,282 (1931). Cf. also Carbo-Norit-Union Verwaltungs-G.m.b H., Ger. Pat. 543,015 (1929).

[443] Kazachkov, L. I., *J. Chem. Ind. (U.S.S.R.)*, **8**, 720 3 (1931); *Chem. Abs.*, **26**, 1754 (1932).

[444] Ruff, V. T., and Martynova, O. I., *Vodosnabzhenie Sanit. Tekh.*, **3**, No. 10, 74–84 (1938); *Khim. Referat. Zhur.*, **2**, No. 3, 102–3 (1939); *Chem. Abs.*, **34**, 1105 (1940).

[445] Rutovskiĭ, B. N., *J. Chem. Ind. (U.S.S.R.)*, **12**, 940 (1935).

[446] Metallges. A.-G., Ger. Pat. 598,852 (1934).

[447] I. G. Farbenindustrie A.-G., Brit. Pat. 448,712 (1936); Fr. Pat. 795,038 (1936).

[448] Otto, C., and Co., Ger. Pats. 543,791, 573,-103 (1929). Klär- u. Entphenolungs G.m.b.H., Fr. Pat. 703,721 (1930). Holmes, W. C., and Co., and Cooper, C., Brit. Pats. 372,399 (1932), 407,801 (1934).

[449] Gibbons, M. M., *Ind. Eng. Chem.*, **24**, 977–82 (1932). Lagergreen, A., *Tek. Tid.*, **63**, 217 (1933); *Chem. Zentr.*, **104**, 1423 (1933). Baylis, J. R., *Elimination of Taste and Odor in Water*, McGraw-Hill Book Co., New York, 1935, Chapters 4–6.

[450] Travers, J. T., Lewis, C. H., and Urbain, O. M., U. S. Pat. 1,850,644 (1932). Norcom, G. D., *Water Works and Sewerage*, **80**, 58 (1933).

[451] Basore, C. A., U. S. Pat. 1,323,239 (1919); Brit. Pat. 139,168 (1920). Baylis, J. R., pp. 84–5 of ref. 449.

[452] Brown, R. L., *Am. Gas Assoc. Monthly*, **8**, 211–14, 240, 254, 279–82, 302 (1926).

black retained its activity. He considered the process expensive on a commercial scale. Basore [451] combined his bone-black filtration with other purification processes, including aeration of the hot liquor, and filtration through spent slag, which eliminated some sulfides and cyanides.

Davis and Semenow [452, 453] found that a large portion of the phenols were removed from still waste in trickling through a bed of lignite; 15 parts of lignite were used per 100 parts of waste. The lignite was revivified for further use by standing under proper conditions. A revivification required about 3 weeks, but the number of revivifications was apparently limited. It was concluded that the possibilities of revivification in a practical way were not great. Peat was used instead of lignite by Dieterle and Semenow.[452, 454] The peat eliminated taste- and odor-producing compounds. Bacterial action was an important factor in these treatments.

Knothe [455] dephenolized low-temperature carbonization liquors by filtering through lignite ash. The use of ashes, brown-coal coke, or active carbon for purifying aqueous liquors from lignite carbonizing operations was recommended by Stooff.[456]

Witt and Schuster [457] removed hydrogen sulfide from a tarry, turbid effluent from lignite carbonization by filtration through low-temperature coke. This was followed by acidification of the liquor with flue gases, and then a second filtration through fresh coke, at the rate of 1 part liquor per part of coke per hour. The effluent had only a faint odor, gave only a slight turbidity with bromine water, and remained colorless after long standing in air. The oxygen-absorbing capacity was reduced by 85 percent.

PRECIPITATION OF PHENOLS WITH LEAD SALTS

Phenols. Phenols have been precipitated from ammoniacal liquors by the addition of lead salts by Urbain.[458] The reaction, he stated, was stoichiometric, and the proper addition was determined by a prior test on the liquor. Thus, 100 parts of phenol required 430 parts of tribasic lead acetate to produce ·337 parts of plumbyl phenolate. The precipitate was separated and treated with 66° Baumé sulfuric acid, and the phenol was distilled off. The lead acetate also precipitated carbohydrates, organic acids, other hydroxybenzenes, and amines. These compounds were burned off the phenol-free sludge to leave a large amount of a white lead sulfate. Any lead acetate left in the ammoniacal liquor was removed by precipitation with sodium sulfate.

Polyhydroxy Phenols. Catechol has been recovered from ammoniacal liquors by precipitation with lead chloride or lead acetate. Before precipitation, the liquor was made slightly alkaline, to pH 8.0, with ammonia. The precipitate of lead catechol was separated by filtration and decomposed with hydrochloric acid. After the lead chloride was removed, the aqueous solution of catechol was distilled under vacuum. Before all the water was off, superheated steam was introduced into the still; and an aqueous solution from which the catechol, m.p. 104° C, crystallized on cooling was obtained. The process was operated by

453 Davis, H. S., and Semenow, S. D., U. S. Pats. 1,323,251 (1919), 1,437,401 (1922); Brit. Pat. 139,159 (1921).

454 Dieterle, E. A., and Semenow, S. D., U. S. Pat. 1,323,256 (1919); Brit. Pat. 152,356 (1920).

455 Knothe, W., Ger. Pat. 506,021 (1929).

456 Stooff, H., *Kleine Mitt. Mitglied. Ver. Wasser-, Boden- u. Lufthyg.,* **6,** 131 (1930); *Chem. Abs.,* **24,** 5091 (1930).

457 Witt, D., and Schuster, F., *Gas- u. Wasserfach,* **71,** 241–4 (1928).

458 Urbain, O. M., U. S. Pats. 1,973,999, 1,974,000 (1934).

Parkes [459] on a semi-commercial scale for purifying low-temperature carbonization liquors containing 2 to 2.5 grams per liter of catechol.

In order to reduce consumption of the lead salt, the liquor was freed from sulfide and carbonate before the treatment. Owing to the extremely small concentration of catechol in the liquors from high-temperature carbonization, the process has not been of interest to operators of such plants. Parkes [459] stated that aluminum, zinc, magnesium, or manganous salts may be used instead of lead. Nitsche [460] patented a process similar to the Robinson process.

REMOVAL OF PHENOLS WITH HALOGENS

The effect of chlorine on phenols in ammoniacal liquors has been studied by Chulkov and coworkers.[461] To a solution containing 10 grams per liter of phenol were added 40 of caustic soda, or the equivalent amount of lime, and 30 grams per liter of chlorine were bubbled in. A resinous product amounting to 7 grams per liter was produced which proved to have value for use in paints and lacquers. Chulkov combined his chlorination treatment with other processes, including prior treatment of the liquor to remove compounds which react with chlorine, such as sulfides. The excess chlorine was removed by aeration, and the liquor was filtered through active carbon to produce a colorless, odorless, phenol-free liquor. Chlorination of ammoniacal liquors containing higher concentrations of caustic soda first produced mono- and dichlorophenols. With further treatment trichlorophenol was produced, but eventually this was completely broken down.

In his experiments, Todd [462] found that phenols in water were oxidized to tasteless products by chlorination at a pH of 5.7 or less. Ferrous sulfate was added to coagulate any precipitates. Bromine was used by Rose [463] to produce solid products by reaction with the phenols in ammoniacal liquors. The suspension was removed by flotation. Durand [464] used hypochlorite for purification of coke-plant waste waters which were killing fish in the Marne. Hydrogen sulfide and hydrogen cyanide were completely eliminated.

The use of chlorine for elimination of phenolic tastes in water supplies has been described by Baylis.[465]

An ammonia-chlorine process is used in water-purification practice to prevent the formation of tastes which would be produced in water containing traces of phenol by treatment with chlorine alone. In experiments at Cleveland ammonia in a concentration of 0.25 part per million was added to filtered water before chlorination. In the presence of 0.1 to 0.5 part per million of phenols and of 0.2 to 0.5 part per million of chlorine, effective sterilization was secured without producing phenolic tastes.[466] The increased costs were very low.

459 Parkes, D. W., *J. Soc. Chem. Ind.*, **48**, 81-6T (1929) ; U. S. Pat. 1,821,815 (1931) ; Brit. Pat. 305,494 (1927). Monkhouse, A. C., *Gas J.*, **191**, 153 (1930) ; *Gas World*, **93**, 81 ; *Iron & Coal Trades Rev.*, **121**, 423 (1930) ; *Trans. 2nd World Power Conf., Berlin*, **2**, 75–89 (1930).

460 Nitsche, P., Ger. Pat. 532,178 (1927).

461 Chulkov, Y. I., *J. Chem. Ind. (U.S.S.R.)*, **11**, No. 12, 48–59 (1934) ; *Chem. Abs.*, **29**, 2269 (1935) ; Russ. Pat. 39,688 (1934) ; *Chem. Abs.*, **30**, 3560 (1936). Chulkov, Y. I., Parini, V. P., and Bol'ko, S., *Org. Chem. Ind. (U.S.S.R.)*, **1**, 481–4 (1936), **3**, 97 (1937), **5**, 277–82 (1938) ; *Chem. Abs.*, **30**, 6864 (1936), **32**, 8112 (1938).

462 Todd, A. R., *West Va. Univ. Coll. Eng., Tech Bull.* **11**, Series 39, No. 4-I (1938), pp. 18–20.

463 Rose, H. J., U. S. Pat. 1,840,977 (1932).

464 Durand, R., *Bull. sci. pharmacol.*, **30**, 216–19 (1923) ; *Eau*, **10**, 115 (1923).

465 See Baylis, J. R., Chapter 13 of ref. 449.

466 Braidech, M. M., *Ohio Conf. Water Purification, Ann Rept., 9th Rept.* (1929), pp. 67–88. Hatch, B. F., *Blast Furnace & Steel Plant*, **18**,

REMOVAL OF TAR ACIDS WITH FORMALDEHYDE

The well-known reaction of formaldehyde with phenol to produce resins has stimulated investigation of this method of dephenolization. Bunge and Macura [467] patented the treatment of ammoniacal liquors with aldehydes, such as formaldehyde or furfural, preferably with heating, by which a resinous condensation product was formed. It was proposed that flocculating agents could be added to remove the suspended phenolic compounds. Low Temperature Carbonization, Ltd., [468] has also patented the use of formaldehyde.

Formaldehyde or its polymers have been used for similar treatment of the liquor from brown-coal carbonization. [469] Siverteev and Aleksandrovich [470] completely removed phenols from an aqueous liquor from Gdov shales by heating with a small amount of formaldehyde and about 3 percent of sulfuric acid at 100° C. Boiling the acidified liquor with a little pine sawdust removed 95 percent of the phenols. The furfural, formed by hydrolysis of the woods, condensed with the phenols in a similar manner to formaldehyde. [470]

RECOVERY OR ELIMINATION OF CYANIDES AND THIOCYANATES

Thiocyanates. Since ammoniacal liquors from coke plants contain only about 2 grams per liter of thiocyanates, it has not paid to treat them directly for recovery of these salts. [471] In 1863, Spence [472] proposed separating the thiocyanates, in the form of cuprous thiocyanate, by adding cupric and ferrous sulfates to the liquor after the free ammonia had been removed by distillation. Although this idea has been revived in various forms since that time, it does not appear to have become of any importance. Storck and Stobel [473] acidified ammonia liquor with hydrochloric acid and then precipitated cuprous thiocyanate by the addition of a mixture consisting of cuprous chloride and sodium bisulfite. The precipitate was washed, then boiled with a barium hydrate solution, and the barium thiocyanate allowed to crystallize.

Parker and Robinson [474] added cupric sulfate to the ammonia liquor and then carried out the necessary reduction by passing sulfur dioxide through the solution. The excess cuprous sulfate was recovered. The cuprous thiocyanate was converted to ferrous thiocyanate, and the copper was recovered by the addition of metallic iron, according to Bower. [475]

Crowther [476] recovered the thiocyanates from still waste. The lime was first precipitated with carbon dioxide. A paste of cuprous oxide was then added to the clear liquor, and the mixture made slightly acid with hydrochloric acid. The cuprous thiocyanate was filtered off and converted to other salts by the addition of alkali carbonates or hydroxides. The cuprous oxide was recovered.

618–9, 621 (1930). Baylis, J. R., Chapters 10–12 of ref. 449.

467 Bunge, F. C., and Macura, H., Ger. Pat. 505,570 (1927) ; Brit. Pat. 326,112 (1929) ; Fr. Pat. 676,871 (1929).

468 Low Temperature Carbonization, Ltd., and Flack, N., Brit. Pat. 443,899 (1936).

469 Kohlenveredlung u. Schwelwerke A.-G., Ger. Pat. 567,625 (1933).

470 Sivertsev, A. P., and Aleksandrovich, D. A., Org. Chem. Ind. (U.S.S.R.), 4, 281–4 (1937) ; Chem. Abs., 32, 2330 (1938). Aleksandrovich, D. A., Russ. Pat. 46,930 (1936) ; Chem. Abs., 33, 3568 (1939).

471 Shnidman, L., Proc. Am. Gas Assoc., 1932, 950–69.

472 Spence, P., Brit. Pat. 2,364 (1863) ; Chem. News, 18, 119 (1863).

473 Storck, F., and Stobel, C., Dinglers polytech. J., 235, 157–8 (1880).

474 Parker, T., and Robinson, A. E., Brit. Pat. 2383 (1890).

475 Bower, H., Brit. Pat. 361 (1896).

476 Crowther, H. W., Brit. Pat. 11,964 (1898).

Cyanide. The low concentration of cyanide in ammoniacal liquor has rendered its recovery uninteresting also, although several methods have been proposed. Heffner and Tiddy [477] washed the gases leaving an ammonia still with a solution of caustic soda and recovered the cyanide. The use of a solution containing an alkali hydroxide or carbonate and an iron salt has been patented.[478] The final product was a ferrocyanide. Denis [479] converted the cyanide to ferrocyanide by the addition of an alkali and ferrous sulfate directly to the liquor.

The gradual oxidation of cyanide to thiocyanate in the liquor has been utilized by Schönfeld [480] for elimination of the cyanide. The liquor was treated with sulfur or sulfides in the presence of catalysts, such as active carbon or silicic acid. Colman and Yeoman [481] suggested that cyanide be converted to thiocyanate by passing air with the steam through the still. In a week's operation, the cyanide content of the crude, concentrated liquor produced in the still had dropped from 0.83 to 0.304 gram per liter, calculated as ammonium thiocyanate.

The Noerdlingers [482] removed both cyanide and thiocyanate together from the liquor. After acidification of the liquor with an acid other than nitric, an oxidizing agent, such as manganese dioxide, was added, which converted the thiocyanate to cyanide. The cyanide was removed with a current of air and was recovered by washing the air with a suitable reagent. As little as 0.25 gram per liter of thiocyanate was removed in this way.

In the investigation made by Southgate and his coworkers [483] on the poisoning of smelt in the Tees Estuary, methods for removing the highly toxic cyanides from the waste waters of coke plants were studied. The cyanide, present in concentrations of about 40 parts per million, could be considerably reduced by spraying the liquor at a temperature of 58° C into the air as a fine mist. Cyanide was also converted to nontoxic ferrocyanide by the addition of ferrous chloride, available as a slightly acid solution of pickle liquor. Hydrogen sulfide interfered, because it formed ferrous sulfide, which reacted more slowly. Laboratory experiments indicated that an effluent containing not over 40 parts per million of hydrogen sulfide could be treated successfully by mixing for 15 minutes with 300 and 130 parts per million of calcium oxide and ferrous chloride, respectively.

The addition of formaldehyde to convert the cyanide into cyanhydrin usually made the effluent nontoxic.[483] Garner and Wishart [484] found that addition of formaldehyde to a liquor removed thiocyanate and sulfides but had little effect on phenols.

Gases containing carbon dioxide, Neuwirth [485] found, will liberate hydrogen cy-

[477] Heffner, L. W., and Tiddy, W., U. S. Pat. 1,600,288 (1926).

[478] Die Directrie van de Staatsmijnen in Limburg, and C. Otto & Co., G.m.b.H., Fr. Pat. 822,955 (1938).

[479] Denis, J., Brit. Pat. 250,824 (1924).

[480] Schönfeld, F., Fr. Pat. 638,035 (1927).

[481] Colman, H. G., and Yeoman, E. W., *J. Soc. Chem. Ind.*, **37**, 319-24T (1918); *Gas J.*, **144**, 567-8 (1918); *Chem. Trade J.*, **63**, 421 (1918).

[482] Noerdlinger, H., and Noerdlinger, F., Ger. Pat. 191,078 (1905); Brit. Pat. 1764 (1906).

[483] Southgate, B. A., Pentelow, F. T. K., and Bassindale, R., *Biochem. J.*, **26**, 273-84 (1932). Southgate, B. A., *Gas J.*, **202**, 216-8 (1933); *Gas World*, **98**, No. 2554, Coking Sect., 56-9 (1933); *Biochem. J.*, **27**, 983 (1933); *Yearbook, Coke Oven Managers Assoc.*, 203-13 (1934). *Dept. Sci. Ind. Research (Brit.), Water Pollution Research, Rept. for the Year Ended June 30, 1933*, 56 pp. Alexander, W. B., et al., *J. Marine Biol. Assoc. United Kingdom*, **20**, 717-24 (1936).

[484] Garner, J. H., and Wishart, J. M., *West Riding of Yorkshire Rivers Board Rept.* **174** (1936), 22 pp.

[485] Neuwirth, F., *Berg- u. hüttenmänn. Jahrb. montan. Hochschule Leoben*, **81**, 126-31 (1933); *Chem. Abs.*, **28**, 2810 (1934).

anide from liquors containing cyanides. Strell [486] reported that the liquor could be acidified and blown with air. ·

The conversion of cyanogen compounds to ammonia by concentrating a solution made alkaline with soda ash has been described by Baker.[487] The liquor was then treated with a compound of a metal other than mercury to precipitate residual cyanide or thiocyanate. Baker also removed cyanide from ammoniacal liquor, from which the free ammonia had been distilled, by the addition of oxides or chlorides of copper, tin, silver, nickel, or aluminum.[488] The precipitate was removed and the liquor treated with unpurified coal gas, hydrogen sulfide, or both, to precipitate any excess of the metallic compounds. The purified liquor was evaporated for the production of ammonium chloride.

REMOVAL OF HYDROGEN SULFIDE

Hydrogen sulfide is eliminated from ammoniacal liquor during distillation in the ammonia still; in the semi-direct byproduct process it is then returned to the gas with the ammonia and other vapors. Addition of a metallic compound to precipitate an insoluble sulfide has been suggested. Falding [489] used pickle liquor to precipitate ferrous sulfide. Enough ferrous sulfate was added to combine with the free ammonia, and iron hydroxide and ammonium sulfate were additional products.

Ammoniacal liquors were treated with lime by Sokolova and Bezuglov.[490] Calcium sulfide precipitated in the sludge. This was treated with flue gases to produce

calcium hydrosulfide, which was filtered off and mixed with an acid solution of sodium sulfate. Free sulfur was liberated.

The Deutsche Ammoniak-Verkaufs Vereinigung G.m.b.H.[491] removed entrained tar from ammoniacal liquor by precipitation of the sulfide with ferric sulfate or zinc sulfate. The tar was entrained by the precipitate and could be filtered out. The use of iron ores for precipitation of an insoluble iron sulfide was recommended by Bezugluii and Ignatenko.[492]

Dieterle and Semenow, and Basore,[493] mentioned filtration of still waste through blast-furnace slag containing iron oxide to remove calcium sulfide. The cyanide was partially removed. Miniovich and Dizhevskii [494] added cupric sulfate to liquor and precipitated cupric sulfide.

Queret [495] desulfurized liquor by oxidation with air in the presence of traces of metallic salts, such as nickel sulfate. An electric current promoted the oxidation. The use of colloidal nickel sulfide as a catalyst in an aeration process has been patented.[496] The I. G. Farbenindustrie [497] passed air through the liquor, and then oxidized the sulfide, ammonia, and cyanide compounds, which were vaporized, by passing the air over catalysts.

Sulfur dioxide has been used for the de-

486 Strell, M., *Gesundh.-Ing.*, **62**, 546 (1939).

487 Baker, H., Brit. Pat. 120,759 (1917).

488 Baker, H., Brit. Pat. 112,329 (1917).

489 Falding, F. J., U. S. Pats. 961,763–4 (1910) ; Brit. Pat. 11,364 (1910).

490 Sokolova, E. A., and Bezuglov, D. V., Russ. Pat. 44,539 (1935) ; *Chem. Abs.*, **32**, 8132 (1938).

491 Deutsche Ammoniak-Verkaufs Vereinigung G.m.b.H., Ger. Pat. 609,170 (1935).

492 Bezugluii, D. F., and Ignatenko, F. A., *Coke & Chem.* (*U.S.S.R.*), **3**, No. 3, 53–60 (1933) ; *Chem. Abs.*, **28**, 2877 (1934).

493 Dieterle, E. A., and Semenow, S. D., U. S. Pat. 1,323,256 (1919) ; Brit. Pat. 152,356 (1920). Basore, C. A., U. S. Pat. 1,323,239 (1919).

494 Miniovich, M. A., and Dizhevskii, Y. F., *Ukrain. Khem. Zhur.*, **5**, 193–203 (1930) ; *Chem. Abs.*, **26**, 1753 (1932).

495 Queret, Y., *J. usines gaz*, **53**, 373–86 (1929).

496 Établissements E. Arnoult, Fr. Pat. 750,662 (1933).

497 I. G. Farbenindustrie A.-G., Ger. Pat. 567,-631 (1926).

struction of hydrogen sulfide in ammoniacal liquor. Sebastian [498] found that, although sulfur dioxide would react with the hydrogen sulfide in ammoniacal liquor to produce sulfur, the major portion of the sulfide was not destroyed when treated in an alkaline solution. By use of an excess of sulfur dioxide, 2 moles per mole of hydrogen sulfide, and acidification, the reaction was completed. He acidified the liquor by the addition of acid phosphate.

Bailey [499] mentioned a plant in which the sulfur dioxide in the waste gas from a Claus kiln was used for neutralization of the liquor. Aeration to remove dissolved hydrogen sulfide and sulfur dioxide followed. Bailey stated that this process, when properly operated, should yield a decolorized effluent.

REMOVAL OF ORGANIC ACIDS

Organic acids have been removed from ammoniacal liquors by passing the liquors through alkali carbonates before removal of the phenols.[500] Carboxylic acids have been precipitated from industrial waste liquors by Urbain.[501] A thionyl aniline was added, which precipitated an insoluble anilide. Organic acids, mercaptans, alcohols, amines, and other oxygen-consuming compounds could be removed by the addition of a thionylaminoacylhalide. This reacted with at least one compound to yield products which reacted with others.

Ruff and Martynova [502] recovered fatty acids from the waste waters produced in peat gas plants by liming the liquors and evaporating. The calcium salts were produced.

OXIDATION OF AMMONIACAL LIQUOR

Air. The high oxygen-absorbing capacity of ammoniacal liquors has attracted the attention of investigators to methods of purification involving oxidation. Air has frequently been tried but has eliminated only a portion of the organic compounds. The use of air to eliminate phenols from waste liquors has been advocated by Schulze-Forster and Haase.[503] From 60 to 70 percent of the phenol was removed from waste liquors containing 1 to 2.3 grams per liter, by vigorous aeration with compressed air for 1 to 2 hours at 85 to 90° C. The organic compounds were both polymerized to difficultly soluble compounds and oxidized, the polymerization especially being favored by higher temperatures. The best results were obtained at a pH of 8 to 10. Filtration of the oxidized liquor proved necessary, because much of the insoluble product was too fine to settle rapidly. Bach [504] has questioned whether such a process could be justified if the costs for compressed air and heat to keep the temperature of the liquor above 70° C were taken into account.

Experiments by Heiduschka and Römisch [505] convinced them of the impossibility of rendering phenols harmless within a reasonable time by oxidation alone. Definite diminution of both phenol and cresols in aqueous solution was obtained by oxidation with air in the presence of iron and copper compounds and metallic oxides.

[498] Sebastian, R. L., U. S. Pat. 1,857,571 (1932).

[499] Bailey, T. L., *Gas J.*, **159**, 213–14 (1922).

[500] Deutsche Erdöl A.-G. et al., Ger. Pat. 573,-500 (1933).

[501] Urbain, O. M., U. S. Pats. 1,935,963–4 (1933).

[502] Ruff, V. T., and Martynova, O. I., *Vodosnabzhenie i Sanit. Tekh.*, **3**, No. 10, 74–84 (1938); *Khim. Referat. Zhur.*, **2**, No. 3, 102–3 (1939); *Chem. Abs.*, **34**, 1105 (1940).

[503] Schulze-Forster, A., and Haase, L. W., *Gesundh.-Ing.*, **56**, 608–10 (1933).

[504] Bach, H., *ibid.*, **57**, 93–4 (1934).

[505] Heiduschka, A., and Römisch, H., *ibid.*, **53**, 53 (1930).

Horowitz-Wlassowa [506] also found that simple aeration had little effect on the phenols in waste liquors. Phenols in liquors, which were aerated in the presence of soil or wood charcoal, were oxidized, and this oxidation he ascribed to catalytic and not to bacterial action.

Ammonia still waste, as it came hot from the still, has been aerated in an aeration tower filled with baffles, coke, or other material, over which the liquor trickled, both by Basore and by Dieterle and Semenow.[493] This treatment caused some concentration of the liquor and volatilization of impurities, and it also resulted in a more ready precipitation of the solids in a subsequent settling. In 24 hours, about 95 percent of the precipitable solids settled out.

Caustic alkalies were added by the Badische Anilin und Soda Fabrik [507] to phenolic liquors before cooling and evaporating in air, in order to prevent formation of a resinous sludge from the phenolic compounds in the liquor cooling tower.

Chulkov and coworkers [508] mentioned successful experiments on the purification of phenol waste waters by oxidation and treatment with lime and calcium chloride. Phenols left in the liquor were adsorbed by activated carbon.

Air was blown through ammoniacal liquor by Jacobson [509] to produce a gas containing nitrogen, oxygen, and ammonia. Any hydrogen sulfide in the gas was oxidized catalytically by means of aluminum oxide. The nitrogen and oxygen in the remaining gases then reacted to form nitrogen oxide in the presence of another catalyst.

Ozone. The use of ozone combined with filtration for the removal of minute traces of phenol, naphthalene, and pyridine was studied by Brown at Milwaukee.[510] He found it usually effective but expensive. Ozonized air was used by Neuwirth [511] for purifying liquors containing phenols and cyanide. The action was slow but could be accelerated by the addition of iron or magnesium salts as carriers of the oxygen. This was done by filling the reaction tower with iron ores. Boulanger and Manderlier [512] used ozone for oxidizing waste waters from coal washeries, etc. Coal dust in the water acted as a catalyst. The use of ozone in purifying ammoniacal liquors has been patented by both Marechal and Leggett.[513]

Electrolysis. The anodic oxidation of phenols in waste waters has been patented by Johnstone.[514] The Bamag Meguin A.-G.[515] has also used electrolysis for purification of waste liquors containing phenols. The impurities were partly precipitated and partly destroyed. Taganov and Novodereshkin [516] added magnesium and sodium chloride to the waste liquors containing phenols which were discharged from producer gas plants, then electrolyzed them. After electrolysis, the solution contained no phenol, but a resinous deposit of

[506] Horowitz-Wlassowa, L. M., *Gas- u. Wasserfach,* **73,** 275–8 (1930).

[507] Badische Anilin u. Soda Fabrik, Brit. Pat. 252,982 (1925).

[508] Chulkov, Y. I., Parini, V. P., and Koslovskaja, L., *Org. Chem. Ind. (U.S.S.R.),* **2,** 476 (1936).

[509] Jacobson, D. L., U. S. Pat. 1,713,045 (1929).

[510] Brown, R. B., *Am. Gas Assoc. Monthly,* **1,** 189–90 (1919).

[511] Neuwirth, F., *Berg- u. hüttenmänn. Jahrb montan. Hochschule Leoben,* **81,** 126–31 (1933); *Chem. Abs.,* **28,** 2819 (1934).

[512] Boulanger, L., and Manderlier, F., Belg. Pat 400,312 (1934).

[513] Marechal, Fr. Pat. 350,679 (1905). Leggett, R. M., U. S. Pat. 1,841,913 (1920).

[514] Johnstone, H. F., U. S. Pat. 2,027,982 (1936).

[515] Bamag Meguin A.-G., Fr. Pat. 743,621 (1933).

[516] Taganov, N. I., and Novodereshkin, V. V., *Org. Chem. Ind. (U.S.S.R.),* **4,** 543 (1937); *J. Soc. Chem. Ind.,* **57,** 244B (1938).

chlorinated organic compounds was obtained. The power consumption amounted to 5.2 kilowatt-hours per kilogram of phenol.

Manganese Dioxide. Manganese dioxide has been used by Wells and Wilson [517] for the elimination of complex organic matter from ammoniacal liquor. Before the liquor passed through the bed of ore, its pH was brought to some value in the range 4 to 9, either by boiling off free ammonia or by the addition of acid. The organic compounds were eliminated without the loss of appreciable quantities of manganese by solution in the liquor.

Potassium permanganate will destroy the organic matter in the liquor, but its application would be expensive.[518]

USE OF FLUE GASES ON STILL WASTES

Waste liquors from the ammonia stills have been treated with flue gases to precipitate excess lime. The calcium carbonate settled out, together with other suspended or colloidal matter.[519] Knothe [520] passed flue gases through still waste to purify it for reuse in ammonia scrubbers.

CHEMICAL PRECIPITANTS FOR PURIFICATION OF LIQUORS

In waterworks practice, precipitants or flocculating agents are successfully used for removing impurities entrained in the water, together with some dissolved compounds. Similar reagents have been tried and a number have proved beneficial in the removal of entrained solid or tarry matter from ammoniacal liquors. With some of these reagents, the concentrations of phenol and of other dissolved compounds have been reduced.

Iron or Aluminum Compounds. Gas liquor has been treated with ferrous sulfate, obtained as spent "pickle liquor," and the precipitated iron hydroxide and sulfide filtered off by the Vereinigte Stahlwerke A.-G.[521] During filtration, a current of air could be passed through the liquid and filtering medium. Iron and aluminum coagulants were dissolved by the Finálys [522] in waste waters containing phenols, and flocculation was accomplished by the addition of oxidizing gases, such as air or chlorine. Part of the phenol was carried down in the precipitate.

Aluminum sulfate was used by Dutton [523] for purifying oily and tarry wastes at one gas plant over a period of 4 years. The liquors were settled and filtered through coke, then treated with about 10 pounds of alum per 50 gallons, and finally filtered through sand. Hurley [524] found that the addition of aluminoferric in amounts up to 15 grains per gallon improved a gas liquor but slightly.

At the water-gas plant at Reading, Pa., the waste liquor was purified by the addition of soda ash and ferrous sulfate, settled, and filtered.[525] A mixture of iron and calcium hydroxides and a catalyst, such as the acid-treated waste dust from cement manufacture, was added by Travers and coworkers [526] to liquor containing phenol, in such proportions that there was present not less than 4.4 grains per gallon of iron

[517] Wells, J. H., and Wilson, P. J., Jr., U. S. Pat 2,132,592 (1938).

[518] Bach, H., *Gas- u. Wasserfach*, **69**, 912–5, 947–52 (1926).

[519] Marsson, M., and Weldert, R., *J. Gasbeleucht.*, **61**, 200 (1918); *J. Soc. Chem. Ind.*, **37**, 402A (1918); *Mitt. Landesanstalt Wasserhyg., Berlin-Dahlem*, **1919**, 237–84.

[520] Knothe, W., Ger. Pat. 506,021 (1929).

[521] Vereinigte Stahlwerke A.-G., Brit. Pat. 405,155 (1934).

[522] Finály, L. de, and Finály, S. S. de, Hung. Pat. 102,744 (1930).

[523] Dutton, L. R., *Gas Age*, **43**, 420 (1919).

[524] Hurley, J., *Surveyor*, **78**, 493–5 (1930).

[525] Taylor, A. C., *Gas World*, **100**, 713–4 (1934).

[526] Travers, J. T., et al., U. S. Pat. 1,754,068 (1930).

hydroxide, 14.8 grains per gallon of calcium hydroxide, and 30 grains per gallon of the catalyst material. The phenols were removed when present in concentrations of about 1 gram per liter.

Phenols, cyanides, pyridine bases, and sulfides were removed from waste waters by Kazachkov [527] by heating with iron hydroxide ore. The ore was regenerated by blowing with hot air or steam.

Lime. Waste liquor from a water-gas plant at Flint, Mich., has been successfully treated with 1,500 pounds of lime per million gallons, settled for 2 hours, and passed through coke filters. Turbidity, color, and oxygen consumed were reduced by 90 to 95 percent. [528]

The Dow Chemical Company removed almost 100 percent of the phenol from a mixture of chemical plant wastes containing 20 to 30 parts per million of phenol. The mixture was limed, settled, and filtered on rotary filters. It finally flowed to a large effluent pond, and from here it was discharged to the river. The overall reduction in phenol ranged from 84.9 to 99.9 percent. [529]

Whipple [530] recommended a procedure which consisted in settling the waste liquor in heated settling tanks, treating with lime, again settling, and finally filtering through coke or sand.

Other Chemicals. Among the chemicals which have been used for coagulating impurities in coke or gas-plant liquors were lime and cupric sulfate. [531] An efficient purification was obtained by adding 3 to 4 pounds of calcium hydroxide and 2 pounds of cupric sulfate per 1,000 gallons. The liquor was settled and filtered through coke. Hurley [532] found that treatment of gas liquor with activated carbon and precipitation with cupric sulfate was not a successful means of purification before it was mixed with sewage.

Colloids in the effluents from the manufacture of briquets are negatively charged and can be precipitated by the addition of magnesium hydroxide. This is formed by the addition of magnesium chloride and lime to the liquor, according to Bähr and Kather. [533] Grossman [534] added barium and strontium carbonates to still wastes in order to remove calcium sulfate.

Compounds toxic to fish in the waste waters from coke plants, blast furnaces, and the like were precipitated by the addition of a solution containing 20 percent mercuric chloride, 8 percent sodium chloride, and 30 percent sodium acetate. [535]

METHODS OF ANALYSIS

Methods of analysis for the compounds in weak ammoniacal liquors and wastes are adaptations of standard methods, and many of them have satisfactorily met industrial requirements for years. The accurate determination of phenols has proved unusually difficult, and many analytical procedures have been developed for determining these constituents.

The analysis of a concentrated liquor is performed by similar methods, except that it is usually run on a weight rather than a volume basis. The sampling procedure is

527 Kazachkov, L. I., Russ. Pat. 28,454 (1932); *Chem. Abs.*, **27**, 3764 (1933).

528 Pollock, J. R., *Eng. News-Record*, **87**, 187 (1921).

529 Harlow, I. F., Powers, T. J., and Ehlers, R. B., *Sewage Works J.*, **10**, 1043–59 (1938).

530 Whipple, G. C., *Rept. of Sewerage Commission to N. J. Legislature*, 1908, pp. 145–69; *Chem. Abs.*, **3**, 89 (1909).

531 Hansen, P., *Am. Gas Light J.*, **104**, 228–9 (1916).

532 Hurley, J., *Surveyor*, **81**, 421 (1932); *Munic. Eng. Sanit. Record*, **89**, 625 (1932).

533 Bähr, H., and Kather, K., *Braunkohle*, **21**, 485–7 (1922).

534 Grossman, J., Brit. Pat. 7932 (1907).

535 Grégoire, A., *Bull. soc. chim. Belg.*, **32**, 230–2 (1923).

more complicated, because evaporation of ammonia must be prevented.

Some comparative analyses on a weak liquor and a concentrated liquor made by 15 different laboratories have been reported by Stone.[536] The differences in results give an idea of the magnitude of the errors.

DETERMINATION OF AMMONIA

Ammonia in a liquor is determined by distillation into standard acid, and titration of the excess acid with a standard alkali. For determining the total ammonia, the fixed salts are decomposed with an alkali before distillation. The free ammonia is determined by direct distillation of the liquor without alkali addition, or by a simple titration if no substances which interfere with the indicator are present.[537, 538, 539, 540] Fixed ammonia is calculated by difference between the total and free. Since concentrated liquors seldom contain fixed ammonia, a direct titration for the free ammonia without distillation is usually satisfactory.

A method which is claimed to require 10 to 15 minutes has been described by Beet and Belcher.[541] The sample is diluted so that the equivalent of 0.2 cubic centimeter is distilled. Approximately 50 cubic centimeters of distillate is collected, and the ammonia is absorbed in a boric acid solution. This is titrated with 0.01 N hydrochloric acid, using an indicator consisting of methyl red and methylene blue dissolved in absolute alcohol. A similar method using boric acid was described by Winkler.[542]

Methods in which formaldehyde is used for determining the ammonia have been described by several investigators.[543] Hexamethylene tetramine is formed with liberation of the acid in accordance with the equation:

$$6CH_2O + 2(NH_4)_2SO_4 =$$
$$(CH_2)_6N_4 + 2H_2SO_4 + 6H_2O$$
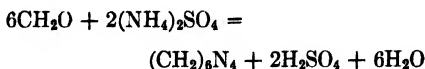
Ten cubic centimeters of the liquor is titrated with 0.1 N sulfuric acid, using methyl orange. The solution is boiled, stoppered, and cooled, and neutralized formaldehyde is added. The final titration of the acid is made with 0.1 N sodium hydroxide, using phenolphthalein.

METHODS FOR PYRIDINE

Pyridine in ammoniacal liquor may be determined by distillation into standard acid and titration, using methyl orange. Since the pyridine will be accompanied by some ammonia, the ammonia must be decomposed by treatment of the distillate with sodium hypobromite. This is done either by passing the vapors from the still through a solution of hypobromite, or by adding hypobromite to the distillate containing ammonia and pyridine. In the second case, after the ammonia is decomposed, the distillate is redistilled.[537, 538, 544, 545]

Rhodes and Younger [546] have described

[536] Stone, C. H., *Proc. Am. Gas Assoc.*, **1923**, 1159–61.

[537] *Gas Chemists' Handbook*, 3rd ed., Am. Gas Assoc., New York, 1929, pp. 348–70.

[538] United States Steel Corp., Chemists' Committee, *Sampling and Analysis of Coal, Coke, and By-products*, 3rd ed., Carnegie Steel Co., Pittsburgh, 1929, pp. 144–62.

[539] See pp. 130–40 of ref. 11.

[540] Bailey, T. L., *Ann. Rept. Alkali, &c., Works*, **64**, 18–30 (1928).

[541] Beet, A. E., and Belcher, R., *Fuel*, **18**, 116–7 (1939).

[542] Winkler, L. W., *Z. angew. Chem.*, **26**, 231–2 (1913); **27**, 630–2 (1914).

[543] Sander, A., *Gas- u. Wasserfach*, **64**, 770–2 (1921); *Gas J.*, **157**, 500–1 (1922). Kolthoff, I. M., *Pharm. Weekblad*, **58**, 1463 (1921); *Chem.-Ztg.*, **46A**, 254 (1922). Meurice, R., *Chem. Trade J.*, **70**, 103 (1922). Stijns, J. H., *Het Gas*, **48**, 540–3 (1928).

[544] Rindin, F., *Am. Gas J.*, **119**, 200 (1923).

[545] Curphey, W. S., *Chem. Trade J.*, **67**, 145–8, 181–5, 221–3 (1920); *Chem. Age (London)*, **3**, 125–6, 155–6 (1920); *Gas J.*, **151**, 179–80, 234–7 (1920); *Gas World*, **72**, 83–6 (1920).

[546] Rhodes, F. H., and Younger, K. R., *Ind. Eng. Chem., Anal. Ed.*, **5**, 302–4 (1933).

an extraction method by which pyridine can be determined in ammoniacal liquors. The liquor is made alkaline with caustic soda and then extracted with successive portions of xylene. From this extract, the pyridine is recovered by a second extraction, using hydrochloric acid. The acid solution is titrated, using a quinhydrone electrode, and the amount of pyridine bases is calculated from the volume of sodium hydroxide added between the two break points on the curve. When pyridine alone was present, these points were found at pH's of 2.8 and 8.5, respectively, but these values may be different when homologs of pyridine are titrated.

DETERMINATION OF SULFIDES, THIOSULFATE, SULFUR, AND SULFATE

Sulfide and thiosulfate are determined simultaneously by running the sample into an acid solution containing an excess of standard iodine. The mixture is back-titrated with thiosulfate, using starch indicator. The sulfides in a second sample of liquor are then precipitated by the addition of lead carbonate. The precipitate is filtered off. The thiosulfate alone will then be determined by an iodine titration. The sulfides may be calculated by difference between the two titrations.[538, 540] The sulfides may also be removed by boiling the liquor before titration for the thiosulfate.[539]

Sulfides are determined directly by adding cadmium chloride solution to the sample. The precipitate is filtered and washed, then dissolved in hydrochloric acid, and titrated immediately with iodine or potassium iodate solution.[537, 538] Meyer and Hempel[547] used a solution of zinc and ammonium acetates in acetic acid to precipitate the sulfides. After washing, the precipitate was dissolved with sulfuric acid and titrated with thiosulfate.

The quantity of volatile sulfur in gas liquor which can be recovered by distillation for use in the manufacture of sulfuric acid has been determined by distilling these compounds into caustic soda. Bromine water in excess was added, and the sulfate formed was precipitated and weighed as barium sulfate.[548]

Total sulfur in the liquor is also determined by oxidizing sulfur compounds to sulfate with bromine. After removal of the organic matter, the sulfates are precipitated and weighed as barium sulfate.[538, 549]

Sulfates alone in the liquor are determined by evaporation of the liquor to dryness. The solids are taken up with dilute hydrochloric acid, and the solution is filtered to remove organic matter. A little zinc oxide is added, the solution filtered again, and the sulfates precipitated as barium sulfate.[538, 547, 549]

DETERMINATION OF CARBON DIOXIDE

Carbon dioxide in ammoniacal liquors is determined by precipitation with ammoniacal calcium chloride. After digestion for 2 hours at 100° C, the precipitate is filtered off, washed, and dissolved in a measured quantity of standard acid. The excess acid is titrated with caustic.[537, 538, 539] Carbon dioxide has also been precipitated with barium hydrate. Sulfites and thiosulfates are oxidized by boiling the solution. The precipitate is separated by filtration and taken up with standard acid. The excess acid is titrated.[538]

To use in control work in the vapor recirculation dephenolizing process, the Koppers Company[550] has modified an old Se-

547 Meyer, M., and Hempel, H., *J. Gasbeleucht.*, **51**, 381-7, 403-9, 425-8 (1909).

548 South Metropolitan Gas Co., *J. Soc. Chem. Ind.*, **56**, 114-5T (1937).

549 See pp. 1266-91 of ref. 67.

550 Shaw, J. A., private communication, 1941.

met-Solvay method for determining carbon dioxide. The sample of liquor is acidified, and the gases are boiled into a buret. The carbon dioxide in the buret is absorbed by bubbling the mixture through a gas analysis pipet, and the contraction is measured. Errors due to the presence of hydrogen sulfide or thiosulfate are avoided by the addition of a little iodine or cupric sulfate to the liquor before removing the carbon dioxide.

DETERMINATION OF CHLORIDES

Chlorides are determined by titration with silver nitrate. Cyanides and organic matter, which would interfere with the end point, must first be removed. This is done by boiling the sample with hydrogen peroxide. When oxidation of the organic matter is complete, the excess peroxide is decomposed by boiling with a little dichromate. The solution is then just neutralized with nitric acid and titrated with silver nitrate.[538, 539]

Thirty percent hydrogen peroxide is used for destroying the organic matter in a modification of this method, developed by the Koppers Company.[550] Traces of peroxide are destroyed, after the addition of a small amount of a chromium salt, by alternating slight acidity and alkalinity of the hot solution. The use of nitric acid for destroying the organic matter is also mentioned.[547]

DETERMINATION OF THIOCYANATES

Thiocyanates are determined by precipitating cuprous thiocyanate, which is filtered from the balance of the solution. The precipitate is decomposed by boiling with sodium hydroxide, and the sodium thiocyanate is titrated with silver nitrate, using ferric sulfate as the indicator, until the red color just disappears.

At the start of the determination, sul-

fides are removed by treatment with lead carbonate, and cyanides and ferrocyanides by precipitation as Prussian blue. The precipitates are filtered off. Ferric iron is reduced to ferrous by the addition of sodium sulfite and boiling. On the addition of cupric sulfate, the cuprous thiocyanate precipitates.[538, 539, 540]

In a modification of this process described by Shaw,[551] the precipitate of cuprous thiocyanate is boiled with bromine water. This oxidizes the thiocyanate with formation of sulfate, which is precipitated and weighed as barium sulfate.

Travers and Avenet[552] recommended boiling the precipitate of cuprous thiocyanate with hydrogen peroxide to oxidize the cuprous copper to cupric. The cold mixture is then titrated with potassium permanganate in the presence of sulfuric acid, whereby the thiocyanate is converted to cyanide, which does not react further, and the sulfur is oxidized. A second method is to oxidize the thiocyanate to cyanide and sulfate by treating with sodium peroxide in alkaline solution at 0° C. The cyanides are distilled into caustic soda and titrated in ammoniacal solution with silver nitrate.

Methods have been described by Weisser[553] and by Strell[554] for determining thiocyanates colorimetrically by formation of the red color with ferric iron.

DETERMINATION OF CYANIDES

Cyanide is determined, after removal of sulfides, by precipitation with an excess of lead nitrate or lead carbonate. The cyanide is then distilled into a solution of sodium hydroxide. A little potassium iodide is added, and the distillate is titrated with

551 Shaw, J. A., *Ind. Eng. Chem.*, **12**, 676–7 (1920).
552 Travers, A., and Avenet, *Compt. rend.*, **190**, 1015–6, 1128–9 (1930), **192**, 52–3 (1931).
553 Weisser, F., *Chem.-Ztg.*, **36**, 1285–7 (1912).
554 Strell, M., *Gesundh.-Ing.*, **62**, 546 (1939).

0.1 N silver nitrate until a white precipitate of silver iodide forms.[537, 538, 539, 554] In any work on the determination of cyanides, thiocyanates, or ferrocyanides, Williams'[555] book on cyanide chemistry will prove useful.

Cyanide and ferrocyanide may be determined together by using the Prussian blue precipitate from the thiocyanate determination. This is ignited and the ferric oxide weighed.[538] Weisser[553] also described a method for determining cyanide by precipitation as ferrocyanide.

Spielman and Wood[556] converted cyanide to thiocyanate by boiling the liquor with ammonium polysulfide. The content of cyanide was then calculated by difference between the thiocyanate content in the original liquor and that after boiling with polysulfide. Thiocarbonate was also converted to thiocyanate by digesting the liquor at 70-75° C for 45 minutes; it could likewise be determined by the difference between two thiocyanate determinations.

An examination of over 20 tests for cyanides led Childs and Ball[557] to the conclusion that the Prussian blue, thiocyanate, silver nitrate, and phenolphthalin tests were most suitable for use on river or crude waters. The Prussian blue test is specific for concentrations of not less than 4 parts per million. The thiocyanate test, although specific for cyanides and about 5 to 10 times as sensitive as the Prussian blue test, was considered too complicated and tedious. The silver nitrate test, which depends upon the opalescence produced on the addition of excess silver nitrate to a slightly acid solution of a cyanide, is not

specific, because halogen acids and sulfides interfere. The test is sensitive to 0.5 part per million. The phenolphthalin test, which depends upon the production of a red color by the oxidation of an alkaline solution of phenolphthalin to phenolphthalein in the cold and upon the presence of a cyanide and a weak solution of a cupric salt, is also not specific for cyanide. Ferricyanide, halogens, sulfides, and phenol all interfere in various ways. It is sensitive to 1 part hydrocyanic acid in 20 million parts of water. The phenolphthalin and silver nitrate tests were recommended for cyanide concentrations of less than 0.2 part per million.[558]

DETERMINATION OF ORGANIC MATTER IN LIQUORS

The organic matter in ammoniacal liquors is determined by oxidation of an acidified solution with potassium permanganate. A number of different methods are described which differ only in the conditions of the permanganate oxidation. In order to obtain comparative results by a given method, the standardized conditions must be closely adhered to at all times.

In the standard test of the American gas industry,[537] the sample, acidified with sulfuric acid, is digested with an excess of permanganate for 5 minutes at 85 to 90° C. Oxalic acid is used for back titration. The result, expressed as the number of cubic centimeters of 0.02 N potassium permanganate required to oxidize the organic matter in a liter of liquor, is termed the "organic number" of the liquor.

A similar test, used by the American Public Health Association,[559] digests the sample for 30 minutes in boiling water,

555 Williams, H. E., *The Chemistry of Cyanogen Compounds*, P. Blakiston's Sons & Co., Philadelphia, 1915, 423 pp.

556 Spielman, P. E., and Wood, H., *J. Soc. Chem. Ind.*, **38**, 43-5, 369-70T (1919).

557 Childs, A. E., and Ball, W. C., *Analyst*, **60**, 294 (1935).

558 Rickard, R. E., *Mining Mag.*, **59**, 9, 93 (1938).

559 *Standard Methods for the Examination of Water & Sewage*, 8th ed., Am. Pub. Health Assoc., New York, 1936, pp. 136-9.

with a definite strength of permanganate and acid. The results are expressed as parts of oxygen consumed per million parts of liquor.

In the British gas industry,[539, 540] two tests are used, one the 4-hour test at 27° C, the other the 3-minute at 27° C for quick control tests. The name of the test indicates the time and temperature of the permanganate treatment. The results are expressed in parts of oxygen per 100,000 parts of liquor.

Kawe [560] has found that some permanganate was consumed when a pure, dilute solution, acidified with sulfuric acid, but containing no organic matter, was boiled. The manganese dioxide formed accelerated the decomposition and introduced a variable error. If the excess of oxalic acid was added to the sample immediately after heating to the boiling point, lower and more uniform results were obtained.

In the permanganate tests, the organic matter is not all completely oxidized to carbon dioxide and water. Franklin and Silvester [561] and Bailey [562] have shown that, in the 4-hour test at 27° C, 1 gram of phenol required 1.77 to 1.78 grams of oxygen. This is about 75 percent of the theoretical oxygen requirement, 2.38 grams. Thiocyanate was completely oxidized, but only about 85 percent of the thiosulfate was eliminated.[561] The least stable organic compounds are most readily attacked and destroyed, but, on the other hand, some organic matter may not be attacked at all. Thus, Ivekovič,[563] cited urea as a compound which is not affected.

Abbott [564] has developed a method in which hot, concentrated sulfuric acid and potassium dichromate are used. With this drastic treatment, destruction of the organic matter was found to be more complete.

DETERMINATION OF PHENOLS

Accurate determination of the phenols in ammoniacal liquors has been a difficult problem for several reasons.

1. The term "phenols" includes not only phenol itself, but also its volatile homologs, notably the cresols. The compounds present, and their proportions, are seldom known, but all are determined and reported as C_6H_5OH. The reactions of phenol and the cresols with the reagents used in the different tests are not the same. Neither do mixtures act in the same manner as might be predicted from the known reactions of the pure components.[565]

2. Other compounds are present which interfere with the reactions, including ammonia, sulfides, cyanide, thiosulfate, and organic matter.

3. Accurate determinations are required over a wide range of concentrations, from several grams per liter down to several parts per million or even per billion.

4. Phenols are volatile and are lost from solution by exposure to the air. This is a less important factor, and errors from the source may be prevented by keeping sample containers stoppered or by making the liquors alkaline with caustic soda. Phenols in very weak solutions decompose on standing. Decomposition of phenol can be retarded by the addition of sodium hydroxide.[566] Owing to possible bacterial action on highly diluted phenol solutions, it is

560 Kawe, A., *Vorratspflege Lebensmittforsch.*, 1, 557 (1938).

561 Frankland, P. F., and Silvester, H., *J. Soc. Chem. Ind.*, 26, 231–7 (1907).

562 Bailey, T. L., *Ann. Repts. Alkali, &c., Works*, 63, 28 (1927).

563 Ivekovič, H., *Plyn. Voda, zdrav. Tech.*, 17, 408–12 (1937); *Chem. Zentr.*, 109, I, 143 (1938).

564 Abbott, W. E., *Ind. Eng. Chem.*, 19, 919–21 (1926).

565 Shaw, J. A., private communication, 1940.

566 Baylis, J. R., p. 212 of ref. 449.

advisable to analyze solutions as soon as possible and to make up standards daily by dilution of stock solutions.[565]

A phenol determination therefore consists essentially of two parts: first, separation of the phenols from the interfering substances, followed by the actual determination of the amount of phenols present. Although a variety of methods has been used to eliminate interfering compounds, in most tests the phenols are ultimately distilled from the sample before the actual determination.

Methods for determining monohydric phenols may be classified as follows:

1. Bromometric methods.
   a. Titrimetric.
   b. Turbidometric.
   c. Gravimetric.
2. Iodometric methods.
3. Colorimetric methods.
   a. Indophenol colors.
   b. Azo colors.
   c. Tungsten and molybdenum complexes with phosphoric acid.
4. Miscellaneous methods.

The methods aim to include the monohydric phenols, but not the polyhydric compounds which are but slightly volatile with steam. Horn [567] stated that catechol and a little of the naphthol are volatile in steam from acid solution, but most of the naphthol, some catechols, hydroquinone, resorcinol, pyrogallol, and phloroglucinol are not.

On account of the differing reactions of the phenols, variations in the test conditions may cause serious errors in the results. The investigators have endeavored to define conditions under which accurate results on the mixture of compounds may be secured, and in many cases have checked their results on known synthetic mixtures of phenol and cresols. An analyst following a given method should therefore adhere closely to the specifications.

Bromometric Methods. The differences between phenol and the cresols may be exemplified by the reactions which occur in the bromometric titration method. The reactions have been studied by Scott.[568] From the work of various investigators,[569] including Ditz and Cedivoda, Pence, and others, he concluded that o- and p-cresols differ from phenol and m-cresol in tending to form dibromo compounds in contrast to the tribromo compounds formed by the latter two:

$$C_6H_5OH + 3Br_2 \rightarrow C_6H_2Br_3OH + 3HBR$$

$$C_6H_4CH_3OH + 2Br_2$$
$$\rightarrow C_6H_2Br_2CH_3OH + 2HBr$$
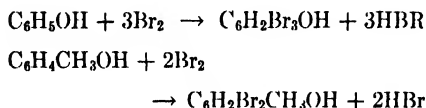
In addition, o- and p-cresols may, in the presence of a large excess of bromine, form tetrabromo derivatives:

$$C_6H_4CH_3OH + 4Br_2$$
$$\rightarrow C_6HBr_3CH_3OBr + 4HBr$$
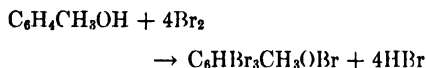
When hydriodic acid is added, the tetrabromo compound may be incompletely reduced to tribromocresol. Since the excess iodine is titrated, it is obvious that different results are possible, depending upon the proportions of the compounds produced.

Scott [568] established specifications for the test, including limitations on the quantity of phenols titrated. When his specifications are used, he concluded that no appreciable error in results would be introduced by the variations in the proportions of phenol and cresols likely to be encountered

[567] Horn, M., *Kleine Mitt. Mitglied. Ver. Wasser-, Boden- u. Lufthyg.*, **5**, 52 (1929); *Chem. Abs.*, **24**, 3304 (1930).

[568] Scott, R. D., *Ind. Eng. Chem., Anal. Ed.*, **3**, 67–70 (1931).

[569] Ditz, H., and Cedivoda, F., *Z. anal. Chem.*, **38**, 873, 897 (1899); *Analyst*, **25**, 74 (1900). Pence, C. M., *J. Ind. Eng. Chem.*, **4**, 518–20 (1912).

in practice. His titration method has been adopted by the American Public Health Association [570] for determination of phenols in concentrations above 10 to 30 parts per million.

In 1876, Koppeschaar [571] first described the bromometric titration method for determination of phenols. The tribromophenols were formed, potassium iodide was added, and the iodine was titrated with thiosulfate. At first, Koppeschaar used bromine water to produce the brominated compounds, but later he substituted a bromide-bromate solution. The bromine evolved was allowed to react with the phenols for 15 minutes. The potassium iodide was added, the solution acidified with hydrochloric acid, and the iodine titrated.

A number of modified methods have been proposed by Scott [568] and by other investigators,[572] and some of them are used for determination of phenols in ammoniacal liquors in American practice. These investigators described specialized treatments for the elimination of the impurities in their methods and have used bromide-bromate solutions. Travers and Avenet [572] distilled the phenols from acidified liquor with superheated steam at 350° C. Sulfides in the distillate were destroyed by the addition of hydrogen peroxide, the excess of which, in turn, was eliminated by neutralization and the addition of traces of cobalt nitrate. The solution was then ready for titration.

Münz [572] purified his liquor by the addition of ammoniacal cupric sulfate, then made it strongly alkaline with sodium hy-

droxide and distilled off the ammonia. The solution was neutralized with carbon dioxide and the phenols distilled off in a current of the gas. The phenols were determined in the distillate. After investigating six methods for phenol determination, Klempt and Ritter [573] concluded that this was the most accurate and reliable and the simplest in operation.

Gösmeier-Kres [574] described two modified Koppeschaar methods. In one the liquor is acidified, cupric sulfate added to react with the hydrogen sulfide, and the phenols distilled off. The concentration of phenols in the distillate is determined either bromometrically or colorimetrically. In the other method, used in the Leuna Works in Germany, the liquor is treated with acetic acid and cadmium acetate to precipitate sulfides. The phenols are then distilled off, and the distillate is made alkaline and extracted with carbon tetrachloride to remove impurities. The extracted liquor is acidified and phenols determined bromometrically.

Phenols were extracted from the sample by Ulrich and Kather [572] with a solution of benzol and quinoline. The extracts were washed with caustic soda, and the phenols were determined in the alkaline solutions by the bromometric titration method. The authors reported that, when a dilute solution acidified with sulfuric acid was allowed to stand in contact with a standard bromide-bromate solution for 1 hour, 3.04 to 3.14 moles of bromine per mole of phenol and the cresols reacted.

Bach [575] used the bromometric titration method without addition of potassium io-

[570] See pp. 253–4 of ref. 559.
[571] Koppeschaar, W. F., *Z. anal. Chem.*, **15**, 233–45 (1876).
[572] Ulrich, F., and Kather, K., *Z. angew. Chem.*, **39**, 229–32 (1926). Rosin, P., and Just, H., *ibid.*, **42**, 965–8, 984–7, 1002–7 (1929). Travers, A., and Avenet, *Compt. rend.*, **190**, 875–6 (1930). Münz, W., *Brennstoff-Chem.*, **12**, 3–4 (1931).

[573] Klempt, W., and Ritter, H., *Ber. Ges. Kohlentech.*, **3**, 302 (1930).
[574] Gösmeier-Kres, E., *Brennstoff-Chem.*, **11**, 369–71 (1930), **17**, 466–70 (1936).
[575] Bach, H., *Gas- u. Wasserfach*, **74**, 331–4 (1931).

dide. The excess bromine was titrated directly.

A standard solution of bromine water has been recommended by Williams.[576] It is added in slight excess, the mixture is allowed to stand for 15 minutes, then potassium iodide is added, and the excess iodine is titrated with thiosulfate. The use of lead carbonate for removal of sulfide prior to the phenol determination is also recommended.

Brominated phenol and cresols are insoluble in water. The turbidity which is produced in a solution of these phenols has been ingeniously utilized for their determination by Shaw.[577] His method has been employed extensively in the United States. Ten cubic centimeters of the liquor is acidified and subjected to a specialized steam distillation. The distillate is divided into portions which are diluted until the concentration of phenols lies between 30 and 35 parts per million; it is brought to 20° C, bromine water is added, the mixture is shaken, and the turbidity is instantly compared with 30- and 35-part-per-million standards. The method is applicable to concentrations down to 75 parts per million, and a modification is available for lower concentrations. A determination by this method is said to take 20 minutes. Rose and Sperr[578] described a method for plant control tests which is similar but dispenses with the distillation. A compact, all-glass apparatus for the distillation has been described by Meanes and Newman.[579]

After investigation of existing methods, the Shaw method was preferred by Kazachkov and coworkers.[580] They recommended that the impurities be precipitated with 5 percent silver nitrate, and the solution be distilled without separating the precipitate.

A gravimetric method for the determination of phenols has been described by the chemists of the United States Steel Corporation.[538] An excess of bromine is added to a sample of the liquor. The solution is acidified and held at a temperature of 70° C for several hours so that reaction is complete. The precipitate is filtered, dried, and weighed. It is considered to be all tribromophenol, and from this weight the concentration of phenol is calculated. The method is stated to give approximate results. In 1910, Autenrieth and Beuttel[581] described a similar method. The solution was shaken for 10 to 15 minutes with an excess of bromine water and allowed to stand for 4 to 6 hours. The authors concluded that each molecule of the precipitate contained four atoms of bromine instead of three. Unsatisfactory results were obtained with o- and p-cresol.

Iodometric Methods. Iodometric methods for phenol determination are based on the work of Skirrow.[582] The phenol is distilled from the gas liquor with water and converted into triiodophenol by treatment of an alkaline solution with a known excess of standard iodine solution. The excess of iodine is titrated with thiosulfate after acidification, and the phenol present is calculated from the iodine consumed. Sulfides and cyanides must be eliminated before the distillation. Cyanides are first converted to thiocyanate by the addition of an excess of ammonium polysulfide.

[576] Williams, R. D., *Ind. Eng. Chem.*, **19**, 530–1 (1927).

[577] Shaw, J. A., *Ind. Eng. Chem.*, *Anal. Ed.*, **1**, 118–21 (1929), **3**, 273–4 (1931).

[578] Rose, H. J., and Sperr, F. W., Jr., *Am. Gas Assoc. Monthly*, **2**, 117–20, 326 (1920).

[579] Meanes, E. A., and Newman, E. L., *Ind. Eng. Chem.*, *Anal. Ed.*, **6**, 375 (1934).

[580] Kazachkov, L. I., et al., *Ukrain. Khem. Zhur.*, **5**, Tech. Pt. 205–23 (1930); *Chem. Abs.*, **25**, 5005 (1931).

[581] Autenrieth, W., and Beuttel, F., *Arch. Pharm.*, **248**, 112 (1910).

[582] Skirrow, F. W., *J. Soc. Chem. Ind.*, **27**, 58–63 (1908).

After the reaction is complete, the excess sulfides are precipitated, most conveniently by treatment with lead carbonate. The lead sulfide and excess carbonate are filtered off; the solution is made alkaline with sodium hydroxide and evaporated until salts begin to crystallize. This removes ammonia and other volatile compounds. After cooling, dilution, filtration, and acidification, the separation of the phenols by distillation is effected. The complete method takes considerable time, but Rose and Sperr [578] recommended it for exact work. The method with slight modifications is used by the gas industry in Great Britain.[539, 540]

In a modification of the Skirrow method,[538] the ammonia is removed in the above manner. The diluted solution is then slightly acidified with nitric acid, and a slight excess of silver nitrate is added to precipitate the sulfides, cyanides, and thiocyanates. The excess silver nitrate is precipitated with chloride. Sodium bicarbonate is added to the filtrate, and the phenols are distilled off. The distillate is also made slightly alkaline with sodium bicarbonate, and excess of iodine is added. After standing for exactly 5 minutes, the solution is acidified with hydrochloric acid and the excess iodine is titrated with thiosulfate. The amount of excess iodine should be carefully regulated.

In this and other modified methods, distillation of the phenols is made from solutions close to neutral, in order to prevent contamination of the distillate with acidic compounds. The pH of the distillate to which the excess iodine is added is also controlled in order to insure that the triiodophenols are formed. In another method,[583] both purified liquor and distillate are buffered by addition of sodium tetraborate. Before the distillation, the liquor is puri-

fied by the addition of cupric sulfate and sodium hydroxide, then boiled to eliminate the ammonia.

Horn [587] described a method of purification in which lead acetate is added to the sample under test. After standing for 24 hours, the filtrate is acidified and distilled until the distillate gives no test for phenol. Calcium carbonate is added to the distillate, and the mixture is redistilled. The final distillate is used for the iodometric titration.

After removal of the impurities, Pieters [584] added disodium phosphate to the solution, and then an excess of 0.1 N iodine solution. After 20 minutes, the excess iodine was titrated.

Dehe [585] recommended that the sample be purified by the addition of zinc acetate solution, silver nitrate, and sulfuric acid, and shaken for 3 to 5 hours. The mixture is filtered, a few drops of hydrogen peroxide added, and the solution steam-distilled until all phenols are over. The distillate is then made alkaline with caustic and evaporated. The residue is dissolved in water, and aliquot portions are treated with standard iodine solution at 50 to 60° C. After cooling, they are acidified, and the excess iodine is titrated with thiosulfate.

Colorimetric Methods. Phenols react with a number of organic compounds to form dyes, several of which have been used to measure quantitatively the phenols present by colorimetric means. These methods have been employed extensively to determine small concentrations of phenols, particularly the low concentrations often encountered in water and sewage. The methods are very delicate, and all-glass apparatus is essential.

[583] Private communication, 1933.

[584] Pieters, H. A. J., *Chem. Weekblad*, **26**, 286 (1929), **27**, 334–7 (1930), **32**, 508–10 (1935). D'Ans, J., *Z. anal. Chem.*, **96**, 1–8 (1934).

[585] Dehe, H., *Chem.-Ztg.*, **52**, 983–5 (1928).

A reagent used widely in the United States is 2,6-dibromquinone chlorimide, which produces a blue color, one of a number known as indophenols. Gibbs [586] investigated these compounds and first described a method for detecting phenols by means of the 2,6-dibromquinone chlorimide. Baylis [587] developed a quantitative procedure, which is now standard with the American Public Health Association.[588]

Gibbs [586] has shown that the pH of the solution is an important factor in the rate of indophenol formation. The most desirable pH appears to be about 9.6, and it should not vary from this value more than about 0.3 pH either way. The pH of the samples and the standards for any one test should not vary more than 0.1 pH. The high buffering which this close control demands is achieved by means of an alkaline sodium borate solution.

Baylis [589] reported that no compounds which give the characteristic blue indophenol color with the Gibbs reagent have been found so far, except phenols. No color is produced by p-cresol, and the reagent is not satisfactory if this compound is present. A yellow color is given by aspartic acid, which has been found in the waste liquors from byproduct coke-oven plants. o-Cresol seems to produce a greater intensity of blue color than pure phenol. Theriault [590] reported that, under certain restrictive conditions in polluted waters, concentrations of 1 or 2 parts per billion have been detected by this test.

Methods for estimating small quantities of phenols in water supplies require the water to be alkaline. Consequently, when more than a few parts per million of calcium and magnesium compounds are present, the samples must be distilled; otherwise precipitates will occur.[588] Distillation also serves to separate phenol from interfering compounds. For determinations on trade wastes, it may be necessary to apply purification treatments similar to those described for the determination of phenols by other methods.

Houghton and Pelly [591] described a colorimetric method by which the phenol is oxidized with hypochlorite in the presence of dimethyl-p-phenylenediamine to an indophenol. They reported that the method is sensitive to 10 parts per billion.

Azo colors have been produced by coupling phenol and diazotized reagents. A method using diazotized sulfanilic acid to produce a yellow to orange color, developed by Fox and Gauge,[592] has been adopted by the American Public Health Association [588] as an alternative to the indophenol test. The color is compared with that of a standard phenol solution.

Donaldson and Furman [593] have described a modified Fox and Gauge method, in which platinum color standards are used. The phenols are distilled from the sample. They estimated that this method gives better than 90 percent of the total phenols present. In another modification by the chemists of the United States Steel Corporation,[538] the phenols are separated if necessary from interfering substances by extracting the sample with ether. The extract is washed in turn with caustic soda solution, and the phenols are determined on the second extract.

[586] Gibbs, H. D., *J. Biol. Chem.*, **72**, 649–64 (1927); *J. Phys. Chem.*, **31**, 1053–81 (1927).

[587] See Baylis, J. R., Chapter 8 of ref. 449.

[588] See pp. 247–51 of ref. 559.

[589] Baylis, J. R., *J. Am. Water Works Assoc.*, **19**, 597–604 (1928).

[590] Theriault, E. J., *Ind. Eng. Chem.*, **21**, 343–6 (1929).

[591] Houghton, A. V., and Pelly, R. G., *Analyst*, **62**, 117 (1937).

[592] Fox, J. J., and Gauge, A. J. H., *J. Soc. Chem. Ind.*, **39**, 260T (1920).

[593] Donaldson, W., and Furman, R. W., *J. Am. Water Works Assoc.*, **18**, 605–20 (1927).

Use of *p*-nitroaniline, which produces a red color, was reported by Hilpert and Gille [594] to give greater accuracy. Thymol was used to prepare the comparison standard.

Nolte [595] found that polyvalent phenols, such as resorcinol, gave the *p*-nitroaniline reaction only in amounts 10 to 20 times those of phenol and cresols. Values obtained by this method corresponded satisfactorily, therefore, with the concentrations of phenols in the sample which were volatile with steam. The *p*-nitroaniline method was reported by Folpmers [596] to give variable results unless precautions were taken to prevent the formation of phenols from traces of organic matter also present. He described a standardized method of avoiding this danger.

Reagents composed of tungsten and molybdenum complexes with phosphoric acid have been proposed for the detection and estimation of phenols by the colors produced. The reagents, first proposed by Folin and Denis,[597] have been widely employed. Since the reagent is very sensitive to mild reducing influences, it is not specific for phenol or for anything except a reducing influence. It is, however, possible by means of this determination to say that phenols are not present above a certain concentration.[550] Procedures for the determination of phenols in water by the Folin and Denis method have also been described by Vorce [598] and by the United States Steel Corporation.[538] The test is sensitive to 1 part per million.

Miscellaneous Methods. The determination of phenols in waste liquors by conductometric titration has been proposed by Lapshin.[599] The sample was acidified with acid, 5 percent in excess of that required for the phenol, cupric sulfate was added to react with hydrogen sulfide, and the solution was distilled. The distillate was then titrated.

Dehe [585] prepared a solution buffered at a pH of 11.04, and then titrated the phenols with $0.1\,N$ sulfuric acid to a pH of 8.4, using phenolphthalein as the indicator.

Odor and taste tests on waters are useful in detecting the presence of phenols, particularly in chlorinated samples.[538, 600]

DETERMINATION OF POLYHYDROXY PHENOLS

Accurate methods for the determination of polyhydroxy phenols in liquors are not available. Several methods have been developed for their estimation, based on the oxygen-absorbing property of catechol, hydroquinone, and pyrogallol, among other polyhydric phenols. Resorcinol, on the other hand, absorbs no oxygen under the same conditions, and its solution remains colorless.[540]

A special Bunte buret [539, 540, 601] is used in one test. A small sample of the liquor, about 15 cubic centimeters, is drawn into this buret and then 6 cubic centimeters of 10 percent sodium hydroxide solution. The contents of the buret are shaken in contact with the air until no further contraction occurs. The contraction is used to calculate the concentration of higher tar acids in parts of oxygen absorbed per 100,000 parts of liquor.

The polyhydroxyphenols have been determined colorimetrically by comparing the

594 Hilpert, S., and Gille, R., *Angew. Chem.*, 46, 326–8 (1933).

595 Nolte, F., *Chem.-Ztg.*, 57, 654 (1933).

596 Folpmers, T., *Chem. Weekblad*, 31, 330–3 (1934).

597 Folin, O., and Denis, W., *J. Biol. Chem.*, 12, 239–43 (1912).

598 Vorce, L. R., *Ind. Eng. Chem.*, 17, 751 (1925).

599 Lapshin, M. I., *Zavodskaya Lab.*, 6, 1455–60 (1937) ; *Chem. Abs.*, 32, 2461 (1938).

600 See pp. 15–9, 126–7 of ref. 559.

601 Bailey, T. L., *Gas J.*, 179, 37–8 (1927).

color of the sample when shaken under standardized conditions in air with that of a freshly prepared solution of catechol made up with similar amounts of ammonia, thiocyanate, and thiosulfate to those in the liquor. The color tints of the unknown and the standard were compared and the results expressed in terms of catechol.[540]

The polyhydroxy phenols have also been estimated from the oxygen absorption of the liquor as determined by the 4-hour permanganate test at 27° C. The oxygen absorptions for the sulfide, phenols, thiocyanate, and thiosulfate, which have been determined by previous analyses, are calculated. When these values are subtracted from the total oxygen absorption, that value which remains unaccounted for is expressed as a "difference" figure. It is due largely to higher tar acids, partly to other substances, and possibly to variations in the oxygen absorptions of the other compounds.[540]

Böck and Lock [602] have described methods for determination of such phenols as hydroquinone, catechol, resorcinol, and others. The hydroquinone is oxidized with ferric chloride in water, extracted with chloroform and benzene, and titrated with iodine. By this method, hydroquinone can be determined in the presence of phenol, resorcinol, and other polyhydroxy phenols, either because the phenols do not give an oxidation product with ferric chloride or because the products are insoluble in chloroform. Catechol must be removed before the test by precipitation with lead acetate. It may be determined in the same way. The concentration in the sample titrated should not exceed 0.05 percent.

In the investigations of Morgan, Pratt

and Pettet,[15, 39] and Gluud,[603] on aqueous liquors from the low-temperature carbonization of coal, the phenols were recovered by extraction with ether. Gluud acidified the liquor with hydrochloric acid, then extracted the ether. Catechol was separated from the extract by treating it with 40 percent calcium chloride solution and concentrated ammonium hydroxide. The aqueous layer was acidified and extracted in turn with ether. The catechol recovered was purified by ether extraction.

Morgan and his coworkers [15, 39] separated the organic matter in low-temperature liquor for analysis and identification of individual compounds by a series of extractions with different solvents. The phenols were extracted with ether from liquor saturated with carbon dioxide. The procedure would be unsuitable for ordinary analytical work.

MISCELLANEOUS ANALYTICAL METHODS

Benzene has been determined in ammoniacal liquor by adsorption on activated carbon, according to Münz.[572] The benzene is then steamed from the carbon and distilled.

Tar in ammoniacal liquor has been determined by Jungblut [604] by extraction, preferably with carbon disulfide. Phenols are removed from the extract by washing with caustic, and pyridine bases by an acid wash. The solvent is then evaporated. A correction to the weight of residue is necessary in order to make up for tarry matter evaporated. Ether is used as the solvent in a similar method by the chemists of the United States Steel Corporation.[538]

Ultraviolet light has been used by Shnid-

602 Böck, F., and Lock, G., *Monatsh.*, **53-4**, 888-96 (1929).

603 Gluud, W., *Ges. Abhandl. Kenntnis Kohle*, **3**, 66-74 (1918).

604 Jungblut, C., *Ann. chim. anal. chim. appl.*, **14**, 337-9 (1932).

man [605] for the analysis of turbid or highly colored solutions, including ammoniacal liquors.

REVIEWS

A number of surveys of the ammoniacal liquor problem have been made, to most of which reference has already been made. Attention should be called to Lunge's *Coal Tar and Ammonia*,[67] because of the comprehensive review of earlier practices in the industry which it furnishes. The British Institution of Gas Engineers has prepared summaries for their transactions, such as the reports of Parker [606] and of Key,[11] and

a report on methods for disposal of the liquor has been made by the French gas industry.[607]

Books which contain information on ammoniacal liquor and its treatment are those of Jacobson [2] and Morgan.[608] Ammoniacal liquor is closely related to the fertilizer industry. Information on fertilizers is summarized annually in the *American Fertilizer Handbooks*.[609]

605 Shnidman, L., *Proc. Am. Gas Assoc.*, 1939, 605.

606 Parker, A., *Gas J.*, 179, 101-3, 172-5 (1927).

607 *Assoc. technique de l'industrie du gaz en France*, Soc. tech. gaz, Paris, 1935, 337 pp.

608 Morgan, J. J., *Textbook of American Gas Practice*, Vol. 1, 2nd ed., Jerome J. Morgan, Maplewood, N J., 1931, 969 pp.

609 *American Fertilizer Handbook*. Published on July 1 of each year by Ware Bros. Co., Philadelphia.

COMBUSTION IN FUEL BEDS

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COMBUSTION ENGINEERING

Of the 450 million tons of coal mined in the United States in 1940[1] about 80 million tons[1] was converted to coke, and only the coke was burned in the fuel beds of blast furnaces, gas producers or generators, or domestic heating units. Of the remainder, perhaps one- or two-tenths is consumed as powdered coal in large utility and industrial power plants; the remainder of all the coal that is mined is burned in fuel beds for the generation of heat, power, or gas. Thus, it is not an exaggeration to say that the great coal industry exists primarily for the purpose of supplying the nation's fuel beds; these necessary adjuncts to an industrial civilization form the subject of this report.

Fuels have been burned in beds since the earliest times; the primitive charcoal fire, made by burning wood in a pit until a heap of glowing char accumulated in it, had all the essential characteristics of a fuel bed. Examples of present-day fuel beds include the open grate fires used abroad for heating and ventilation; heating and cooking stoves and central heating furnaces fired with solid fuels; power boilers, either hand-fired or equipped with stokers —chain-grate, underfeed, or spreader;

blast furnaces, gas producers, and water-gas generators.

Several books on fuels are available, although none is very recent;[2] their existence makes it unnecessary to examine the early literature in detail. Moreover, many journals[3] are devoted almost entirely to one phase or another of the problems of combustion; an exhaustive bibliography would contain practically complete indices to these organs. This has not been attempted; only articles selected from these sources as having special significance are referred to; the diligent worker in this field, however, will find much to repay him for time spent reading through files of these journals.

OPEN FIRES AND GRATES

Open fires have long been customary in Great Britain for most household heating.

[2] Bacon, R. F., and Hamor, W. A., *American Fuels*, McGraw-Hill Book Co., New York, 1922, 2 vols., 1257 pp. Haslam, R. T., and Russell, R. P., *Fuels and Their Combustion*, McGraw-Hill Book Co., New York, 1926, 809 pp. Marcard, W., *Rostfeuerungen,* Ver. deut. Ing. Verlag, Berlin, 1934, 138 pp.

[3] *Combustion; Power; Power Plant Engineering; Fuel; J. Inst. Fuel; Colliery Guardian; Brennstoff-Chem.; Feuerungstech.; Wärme; Braunkohle; Brennstoff- u. Wärmewirt.; Khim. Tverdogo Topliva.* Also large parts of *Mech. Eng.; Heating & Ventilating; Trans. Am. Soc. Mech. Engrs.; Trans. Am. Inst. Mining Met. Engrs.; Engineering; Trans. Inst. Mech. Engrs.; Z. Ver. deut. Ing.; Z. tech. Physik.*

[1] *Minerals Yearbook, Review of 1940*, U. S. Bur. Mines, 1941, p. 768, Table IV.

The standard open fire consists merely of a hearth or basket of iron gratework, set in a fireplace and served by a chimney flue. The chimneys are based largely on designs by Count Rumford,[4] but the grates and hearths in general use apparently "just grew." Britain's blessing of abundant good coal has here resulted almost in a curse; it was so easy to burn the coal available without taking special pains that little attempt was made to improve matters beyond merely satisfactory results. The increasing smoke pall, however, and the need of the gas industry to secure a revenue from the sale of the coke made as a by-product of their gas production has produced, particularly since World War I, a strong organized effort to produce grates on which high-temperature coke can be burned successfully.[5] This has led not only to improved grates, as such, but also to improved ignition means;[6] to fireplaces in which a considerable amount of heat is returned to the room by means of air heated by convection by the flue gas, and to a new model method of investigating fireplace and chimney action.[7]

HAND-FIRED HEATERS AND BOILERS

This classification includes all hand-fired units with enclosed furnaces from the small "cannonball" stove through all the classifications of warm-air furnaces and heating boilers, hand-fired with coal or coke, with heat liberation rates up to about 2 million

Btu per hour; small industrial boilers of the Lancashire type in Great Britain and the horizontal return tubular (H.R.T.) or locomotive types in this country—although many of these are now equipped with stokers; and locomotive and marine boilers, as well as hand-fired water-tube boilers.

These units all have as their basic structure a set of horizontal grates which support the fuel bed and which have openings through them for the passage of primary air for combustion. There is an almost infinite number of grate designs, as every small foundry has developed its own type of grate, but few, if any, have any really outstanding characteristics. Certain features of design are essential; the grate must allow sufficient free cross-sectional area for the passage of the necessary amount of air with the draft available *across the grate*, which is only a fraction of that across the grate and fuel bed; its metal parts must be so designed that they will be adequately cooled by the primary air flowing through the grate at its lowest rating; and it must allow of agitation, or rocking, in order to remove the ash or clinker that is deposited on it as the fuel is burned out, so that the resistance of the fuel bed may be maintained within the proper limits.

Units such as these have all the features which characterize fully developed combustion equipment in greater or less degree. In addition to the fuel bed, they consist of a furnace, totally enclosed, in which the combustion reactions are completed, of heating surface beyond the furnace in which heat is transferred from the hot flue gas to the material to be heated, and of means for the control of the load or rating by control of the flow of air and gas through the unit.

The furnace may be equipped for the admission of secondary air to complete the burning out of the combustible flue gas

[4] Thompson, B., *Essays*, T. Cadell, Jr., and W. Davies, London, 5th ed., 1800, p. 356. See also Rosin, P., *J. Inst. Fuel*, **12**, 198–230 (1939).

[5] Hales, J. S., *Dept. Sci. Ind. Research (Brit.) Fuel Research Tech. Paper*, **46**, (1937), 50 pp. Blackie, A., *J. Inst. Fuel*, **12**, 20–4 (1938). Blackie, A., and Bruckshaw, J. M., *ibid.*, **12**, 24–7 (1938). Moss, W. C., *ibid.*, **14**, 93–7 (1941).

[6] Esselborn, M., *Feuerungstech.*, **27**, 174–5 (1939). Thau, A., *ibid.*, **27**, 175–6 (1939).

[7] Rosin, P., ref. 4.

rising from the fuel bed.[8] The slots in the fire door of a standard heating unit serve this purpose; larger units may be equipped with steam jets or other mechanical means of injecting secondary air into the furnace. Though there are empirical rules for proportioning furnace volume,[9] the available evidence [10] indicates no relation between furnace volume of heating boilers, or its thermal loading, and the liability of such units to objectionable smoke.

The heating surface in such units may consist of convection surface for the transfer of heat to steam or hot water, as in power or heating boilers, or for transfer to circulating warm air for heating; or it may consist of the goods or ware to be heated as in ceramic kilns. In any event, the area for gas flow must be so proportioned that the desired rating may be obtained with the draft available, and, for economical operation, the surface must be adequate to abstract enough heat from the gas to lower the flue gas at exit from the heating surface to a relatively low temperature. The resistance to gas flow through banks of tubes has been quite thoroughly investigated,[11] but the resistance of other arrangements of heating surface is not yet well known. Individual manufacturers of heaters have determined the draft losses through their own units, in which the specific arrangement of surface is known, and

these data are published in their handbooks,[12] but the data have not been reduced to a general formulation. Methods for predetermining the draft loss in kilns and furnaces in which the ware is directly exposed to the heating gases are not known.

Control of the air and gas flow through such small heating units is usually accomplished by means of dampers and adjustable doors. Some kilns have no such provision; the entire control then depends on proper placing of the coal in firing.[13] Proper manipulation of the controls is essential for the successful firing of small units. The care, maintenance, and operation of such control devices are discussed in various operating manuals and instruction books.[14]

Successful operation of hand-fired units depends primarily on the skill with which they are fired. For small, low-rated units, such as those for domestic heating, two general methods of firing bituminous coal are recommended, namely, alternate and cone firing. In alternate firing [15] the bed of hot coke remaining from previous firings is raked to one side of the firebox, and fresh coal is charged in a pile on the other side so that it may be coked by heat radiated from the freely burning coke. It is essential for economical, smokeless operation that a considerable area of ignited coke be left uncovered to assure the combustion of the volatile matter of the coal being coked.

8 Blizard, J., Nell, J., and Houghten, F. C., U. S. Bur. Mines, Tech. Paper **303** (1922), 56 pp. Brooks, H. W., Orr, M. L., Myler, W. M., Jr., and Herbert, C. A., J. Am. Soc. Heating Ventilating Engrs., **31**, 185–214 (1925).

9 Carr, H. R., Power, **79**, 596–7 (1935).

10 Cross, R. C., Sherman, R. A., and Ostborg, H. N., A Field Survey of the Relation of Combustion Space and Setting Height to Smoke When Firing Bituminous Coal with Underfeed Stokers, Battelle Memorial Institute, Columbus, Ohio, 1939, 33 pp.

11 Pierson, O. L., Trans. Am. Soc. Mech. Engrs., **59**, 563–72 (1937). Huge, E. C., ibid., **59**, 573–81 (1937). Grimison, E. D., ibid., **59**, 583–94 (1937). Bohm, J., Wärme, **62**, 425–31 (1939).

12 Heating, Ventilating, Air Conditioning Guide, 1942, Am. Soc. Heating Vent. Engrs., New York, 1942, 1160 + 91 pp. See especially pp. 179–96, 244–6, and 371–5.

13 Rice, W. E., and Austin, C. R., U. S. Bur. Mines, Tech. Paper **598** (1939), 34 pp. Fox, J., J. Inst. Fuel, **12**, 257–80 (1939).

14 Beck, C. V., Modern Combustion, Mid-West Coal Retailer, Chicago, 1931, pp. 200–13. Liebetanz, R., Feuerungstech., **25**, 300–1 (1937). See also pp. 160–5, 168–72, 179–82, 647–96, 988–1014 of ref. 12.

15 Anon., Fuel Engineering Data, Appalachian Coals, Inc., Cincinnati, 1936, Sect. IV, p. 5.

In firing by the conical method,[16] which is said to be applicable especially to low-volatile coal, the coke remaining from a previous firing is broken up and distributed to the sides of the fuel bed, and fresh coal is charged in a conical pile in the center of the bed. Here, again, the ignited coke must be left uncovered, in a ring extending around the cone, to assure the combustion of the volatile from the fresh charge. Of course, in firing anthracite coal or coke it is unnecessary to take these precautions; the fresh charge is simply fired uniformly on top of the bed. It is advisable, however, if the whole surface of the bed is covered, to open the drafts and allow the fire to "come up" until flames break through the top of the bed in order to avoid danger of gas entering the heated space or of "puffs" or slight explosions. Since about 1935 there has been considerable development of stoves and heaters for the smokeless hand-firing of bituminous coal.[17] In all these units the volatile portions of the fuel are drawn through part of the actively burning fuel bed so that they may be completely burned. Many of the units have hopper or magazine capacity enough so that coal for a relatively long period may be fired at one time.

In hand-firing larger units, such as small industrial boilers, locomotives, and marine boilers (except those known as Western River boilers), good practice dictates keeping a light fire, and firing little and often.[18] Each scoopful of coal is spread out thin and is fired in such a way as to cover any thin spots that may be developing. In this way, a light even bed is maintained which is uniformly bright all over.

Among fuel beds that are fired intermittently from the top and thus are similar to those considered above, even though the firing may be done mechanically, may be included those of foundry cupolas and blast furnaces [19] and gas producers and water-gas generators.[20]

CHAIN- OR TRAVELING-GRATE STOKERS

Chain- or traveling-grate stokers are extensively used in this country and abroad for firing free-burning fuels, such as anthracite,[21] coke (usually in the small "industrial" sizes), and the lower-rank bituminous coals and lignites; they are also used abroad and, to some extent in this country, for firing high-rank coking bituminous coals. They are made in various sizes, up to grate areas of about 400 square feet, in single units, and in Great Britain, to 37 feet wide by 22 feet long, in double units. The older, natural-draft units were limited to ratings of about 15 pounds of coal per hour per square foot of stoker area, but the modern forced-draft types, like that in Fig. 1, are capable of ratings up to perhaps 40 pounds per square foot per hour.[22] Such stokers are especially well adapted to the use of coals having relatively high ash content and low ash-fusion temperature because there is slight danger of serious clinker trouble since the fuel bed is little disturbed in its passage through the furnace.

In this type of stoker, the fuel is fed from a hopper onto a continuously moving

16 *1941 Manual of Ordinances and Requirements*, Smoke Prevention Assoc. of America, Chicago, 1941, 176 pp. See pp. 30–1.

17 Fellows, J. R., *Mech. Eng.*, **61**, 278–80 (1939). See also pp. 87–91 of ref. 16. Piersol, R. J., pp. 84–7 of ref. 16.

18 Kreisinger, H., *U. S. Bur. Mines, Tech. Paper* **80** (1916), 83 pp.

19 See Chapter 24.

20 See Chapters 36 and 37.

21 Johnson, E. B., *J. Inst. Fuel*, **12**, 177–97 (1939).

22 Presser, H., *Gluckauf*, **65**, 981–91 (1929); *Arch. Wärmewirt.*, **18**, 239–42 (1937).

grate made up of chain or grate elements linked together to form a continuous loop passing over sprockets at either end of the furnace. The depth of the fuel on the grate is regulated by the position of a gate, or guillotine door, immediately back of the hopper. This is one of the most important adjustments in the operation of these stokers, and many writers have considered the

sion of fuel into heat are given in published descriptions.[25]

The furnaces for such stokers have, in the past, generally been built with long rear and front arches to secure adequate mixing of the streams of gas from the ends of the stoker. The gas from the front end generally is rich, containing large amounts of volatile matter; that from the rear end,
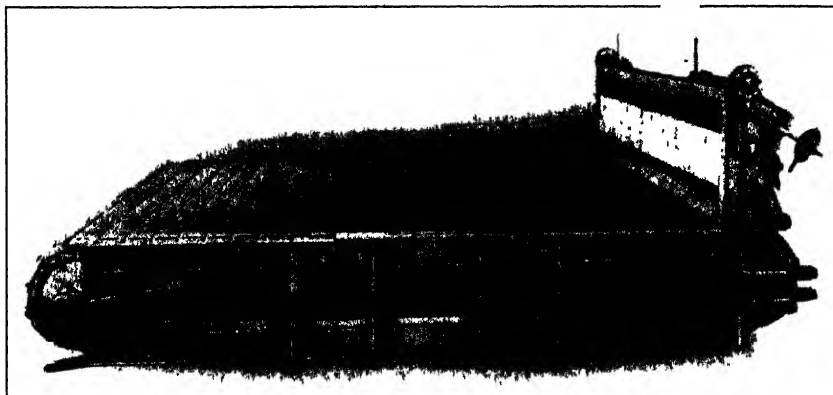
FIG. 1. Forced-draft chain-grate stoker.

proper depth of bed for various conditions.[23] Heavier fires are carried in this country than are customary abroad with free-burning fuels, but in burning coking coals in Great Britain, much deeper fires are carried. Tempering of the fuel, that is, the addition of moisture to it, appears to be necessary or, at least, beneficial, in securing satisfactory operation with these stokers.[24] A great deal of work has been done on the development of the high-capacity traveling-grate stoker, especially in Germany. Details of design to secure a high degree of reliability and high conver-

where the bed does not thoroughly cover the grates, is very lean and contains excess oxygen. The arches throw the streams from the two ends together in the hot part of the furnace so that the lean and rich gases are mixed and serve to correct each other's deficiencies by the ensuing reaction. Modern practice, however, tends to favor relatively smooth furnace walls, with, perhaps, only a short ignition arch at the front of the stoker. The required mixing of the furnace gases is secured by means of relatively small jets of secondary air under

23 Wood, W. H., *Combustion*, **6**, No. 3, 27–30 (1934). Dunningham, A. C., and Grumell, E. S., *J. Inst. Fuel*, **12**, 87–95 (1938). Park, W. M., *Combustion*, **11**, No. 10, 24–8 (1940).

24 Kuss, R. H., *Power*, **81**, 674–5 (1937).

25 Schultes, W., *Arch. Wärmewirt.*, **16**, 117–8 (1935). Schulte, F., *Z. Ver. deut. Ing.*, **80**, 1237–41 (1936). Cleve, K., *Feuerungstech.*, **25**, 317–22 (1937). Mayer, A. R., *ibid.*, **26**, 148–50, 201–11 (1938). Beck, K., *Arch. Wärmewirt.*, **20**, 93–8, 301–6 (1939).

rather high pressure, injected at an angle below the horizontal from either the front or the rear wall.[24]

The conditions within the beds of traveling-grate stokers have been determined experimentally.[26] These investigations show that the layer of coal entering the furnace is ignited at the top of the bed, and that

the fire should be operated so that all the fuel is burned out of the refuse short of the end of the grate, but the air quantity passing through this end of the grate must be controlled to prevent excessive losses.

The temperature reached by the grate elements is of extreme importance in determining their life and freedom from
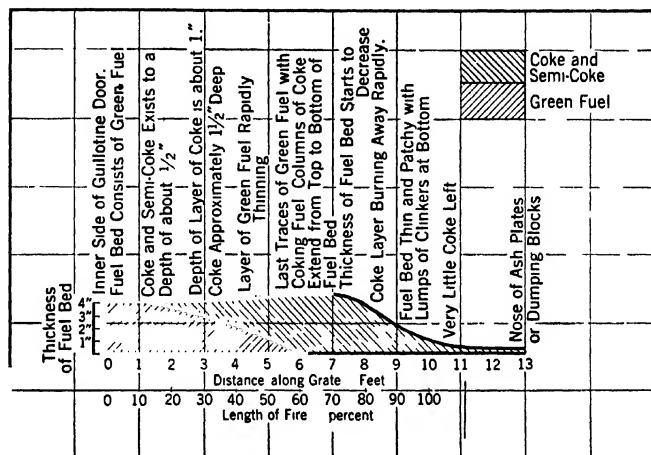
FIG. 2. Example of section through fuel bed of a traveling grate stoker. Maughan, Spalding, and Thornton.[26]

the surface dividing ignited from raw coal moves down as the layer passes through the furnace, as shown in Fig. 2. The ignition surface reaches the grate at the point where observation of the fire during operation shows that the dense flame of volatile matter stops; all the fuel has been ignited and coked at this point, and only the coke residue is burned out beyond it. As this process proceeds, a larger and larger proportion of the bed becomes ashy refuse;

maintenance expense. It has been found [27] that the maximum temperature depends, in a rather surprising fashion, on the rate of primary air flow through the stoker in the region in which the ignition zone is traveling downward; the air rate in the burning-out zone is also important in that, the greater it is, other things being equal, the lower is the maximum temperature reached. In Dunningham and Grumell's work, the maximum grate link temperatures were found for an ignition air rate of 200 pounds per square foot per hour, independent of the size of the coal or its reac-

26 Werkmeister, H., *Arch. Wärmewirt.*, **12**, 225–32 (1931). Maughan, J. D., Spalding, H. B., and Thornton, B. M., *Engineering*, **137**, 587–9, 656–8, 669–71 (1934) ; *J. Inst. Fuel*, **8**, 11–20 (1934). Loewenstein, R., *Wärme*, **57**, 97–101, 121–5 (1934).

27 Dunningham, A. C., and Grumell, E. S., *Fuel*, **17**, 327–34 (1938).

tivity or other characteristics. For either higher or lower air rates during the ignition period, the maximum link temperature for a given burning-out air rate fell off. The explanation of this phenomenon is to be sought in the analysis of heat flow in underfeed beds mentioned in a later section of this report. In addition to control by the rate of air flow in the ignition zone, grate temperatures can be reduced by returning ground ashpit refuse under the coal from a special hopper at the front of the furnace.[28]

UNDERFEED STOKERS—MULTIPLE RETORT

In the multiple-retort underfeed stoker, the coal is introduced through horizontal or slightly inclined cylinders into the bottom of sloping retorts between each pair of which are sloping grates or "tuyère stacks." The coal is forced along the retort by secondary rams, rising to levels from 12 inches to 3 feet above the top of the tuyères. After reaching the level of the top of the tuyères, it spreads out and burns in relatively narrow lanes above them.[29] Units of this type have never attained great popularity abroad,[30] although two large recent British installations were of this type.[31] For many years, however, until well along in the development of the powdered-coal furnace, it was the standard American unit for large, high-capacity installations, especially for those using Eastern coking coals. This type of equipment permits high concentration of capacity per unit building volume for steam capacities below half a million pounds per hour, the largest size units for which these stokers have been built, and may be operated at burning rates up to 75 pounds per square foot per hour.[32] They are especially adapted to utilize the coking coals of the eastern United States since the strong fuel-bed agitation which they supply is capable of dealing with large masses of coke, but they are rather sensitive to coal properties and extremely so to operating adjustment. In spite of these general characteristics, underfeed stokers in which the iron parts are water-cooled from the boiler circulation have recently been applied, with considerable success, to the burning of low-rank Middle Western bituminous coals.[33]

Multiple-retort underfeeds are built with several different types of refuse disposal; with deep clinker-grinder ashpits, as shown in Fig. 3, with continuous ash discharge (Fig. 4), and with dump grates (Fig. 5), although the last mentioned are seldom built, nowadays, except for the smallest installations. The grate surface may be water-cooled, as shown in the unit in Fig 6, a relatively recent development. The preceding stage was characterized by air-cooled grate surface in which the air supplied to each 5-foot section or so of each tuyère stack was separately metered and controlled,[32] as shown in Fig. 3. One manufacturer provides a rather long "overfeed" section at the end of the retorts which is equipped with a so-called undulating grate for complete burning-out of the coke and coal discharged from the ends of the retorts (Fig. 4). Furnaces for these

[28] Maughan, J. D., Spalding, H. B., and Thornton, B. M., ref. 26.

[29] Anon., *Power*, **80**, 469–71 (1936). Mayers, M. A., Dargan, W. H., Gershberg, J., Dalway, B. C., Williams, M. J., and Kaiser, E. R., *Trans. Am. Soc. Mech. Engrs*, **63**, 191–211 (1941).

[30] See Schulte, F., in ref. 25.

[31] London Power Company, Battersea Station, 1936; Deptford West Station, 1937.

[32] Hopping, E. L., *Modern Power & Engineering*, **28**, No. 5, 33–6, 38 (1934); *Mech. Eng.*, **56**, 559–60 (1934). Driscoll, J. M., and Sperr, W. H., *Trans. Am. Soc. Mech. Engrs*, **57**, 49–58 (1935). Griswold, A. S., and Macomber, H. E., *ibid.*, **58**, 13–24 (1936).

[33] Worker, J. G., *Steel*, **100**, 52–3 (1937); *Power Plant Eng.*, **41**, 163–5 (1937); *Power*, **81**, 162–3 (1937). Carroll, H. C., *Trans. Am. Soc. Mech. Engrs.*, **63**, 183–90 (1941).
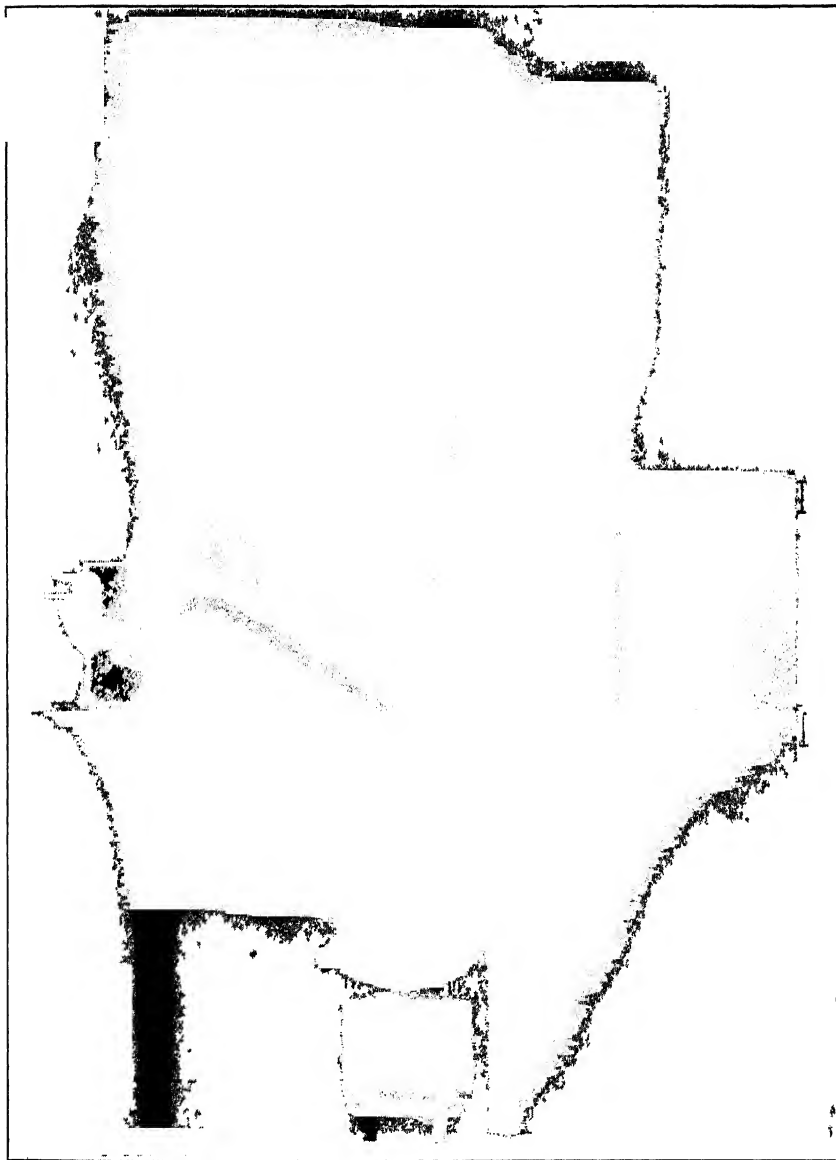
Fig. 3 Multiple retort underfeed stoker equipped with clinker grinder ashpit and zoned air control (Courtesy of the American Engineering Company)

FIG 4   Multiple retort underfeed stoker equipped with link grates and continuous ash discharge
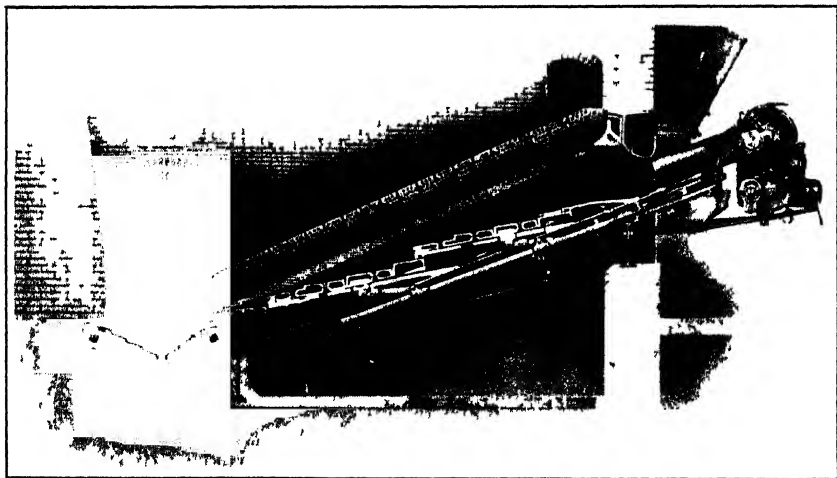
FIG 5   Small multiple retort with dump grates
(Figures 4 and 5, Courtesy of the Westinghouse Electric and Manufacturing Company)

stokers are usually built without arches, as the gases rising from the two ends of the stoker do not differ so markedly in composition as they do in chain-grate-fired furnaces. There is, however, considerable

25 percent in the limiting load that may be carried without objectionable smoke have been obtained by this means.

As mentioned above, these units are quite sensitive to the adjustment of the
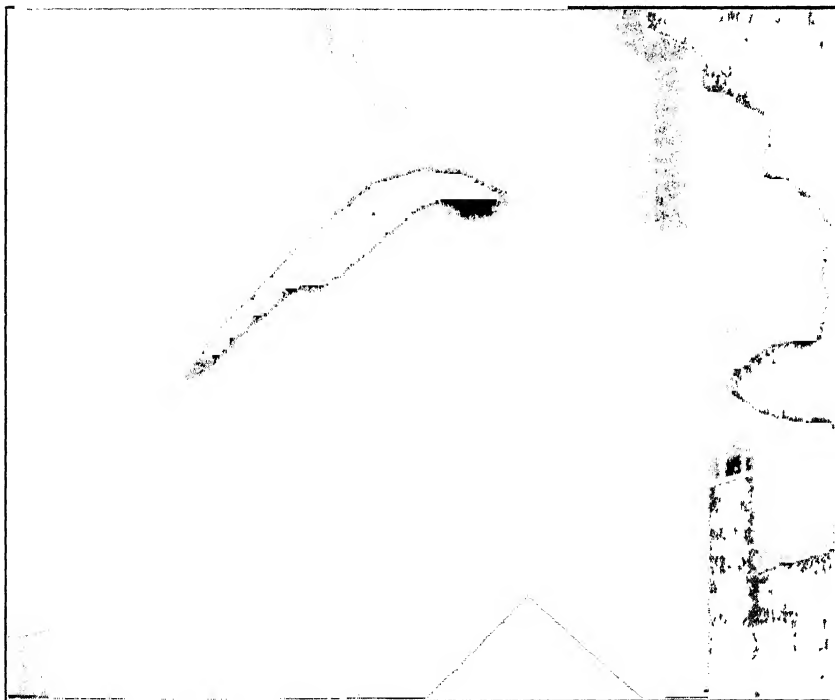
Fig. 6.   Water-cooled multiple-retort underfeed stoker.   (Courtesy of the American Engineering Company)

stratification across the furnace, as the gas rising from the retorts may contain unburned volatile matter and that from the burning lanes may contain unconsumed oxygen. This has led to the application of high-pressure overfire air jets to this type of stoker,[34] also; increases of the order of

various controls and to the type of coal supplied. Many different adjustments are available, including stoker speed, secondary ram strokes, stroke of overfeed section, clinker grinder speed, and air supply to different sections of the grate. These adjustments must be matched to the opera-

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[34] Murphy, B. S., *Trans. Am. Soc. Mech. Engrs.*, **63**, 669–75 (1941). Lawrence, H. F., *ibid.*, **63**, 486–7 (1941). Carroll, H. C., and Clark, R. S., oral discussion, Joint Meeting, Fuel Div. Am. Soc. Mech. Engrs., and Coal Div., Am. Inst. Mining Met. Engrs., Easton, Pa., October 30–1, 1941, Symposium on Operation of Underfeed Stokers.

tion as judged by a skilled stoker tender, from visual observation of the fire. It is this fact that has limited the size of underfeed stokers; when the stoker area increases much beyond 500 square feet, it becomes impossible to see the entire fuel bed so that proper adjustment of the stoker cannot be maintained. According to Clark,[34] one of the principal advantages of overfire air is that it eliminates the necessity of accurate control of fuel-bed conditions by insuring that "popcorn" and combustible gases discharged from the bed will be completely burned in the furnace. It also is possible that the limits on stoker capacity may be raised by raising the average burning rate without raising the rate attained in localized portions of the bed.[35]

UNDERFEED STOKERS—SINGLE RETORT

Single-retort stokers materially antedate the multiple-retort type [36] and have long been used for smaller installations. New interest in this type of unit has developed in the search for a universal stoker for domestic heating. At present these units range in capacity from as low as 10 to above 300 pounds per hour. They vastly outnumber all other types of mechanical burning equipment and account for a large fraction of the 212 million tons of coal [37] consumed annually in industrial plants and for domestic heating.

Single-retort stokers consist of a central "pot" into which the coal is fed, usually by means of a worm working in a tube, but in larger sizes by a reciprocating ram, and in which it rises, meanwhile being coked in

greater or less degree, finally being burned by air issuing from tuyère rings around the top of the retort. Sometimes active grates may be provided outside the tuyère row surrounding the retort; this is almost invariably the case in the larger members of this type. Primary air is almost always supplied under pressure, although in at least one design mechanical draft is supplied for only a small portion of the primary air to insure rapid pickup and secure ignition of the fuel, the principal part of the air being supplied by natural draft through grates surrounding the retort.[10]

Figure 7 illustrates a standard domestic unit for a maximum load of 60 pounds per hour. It has the typical circular pot, and air is supplied only around the top of the retort. It is shown equipped with a "bin-feed" screw, so that coal is brought direct from the bin and fired without the necessity of manual handling. Ash is removed manually, however, in the form of a clinker which collects in a ring around the top of the retort. Control is applied on an off-and-on basis; a thermostat in the living space, when it calls for heat, starts the motor which actuates both the fan and the coal feed screw. Industrial units usually have elongated retorts and active side grates.

Generally, in the designs of domestic stokers, the emphasis has been on mechanical features to assure reliable operation. Relatively little attention has been paid to the characteristics which differentiate combustion from a materials-handling problem, with the result that such units are inclined to be very sensitive to the quality and preparation of the coal supplied. In fact, many coals, considered of premium grade for most other uses, cannot be burned with any success on such stokers. This arises from the fact that the pot-type stoker was originally developed to burn the

[35] Mayers, M. A., *Trans. Am. Soc. Mech. Engrs.*, **63**, 479–89 (1941).

[36] Worker, J. G., and Peebles, T. A., *Mechanical Stokers*, McGraw-Hill Book Co., New York, 1922, 258 pp.

[37] U. S. Census Bur., *Statistical Abstract of the United States, 1941*, Govt. Printing Office, Washington, 1942, Table 828, p. 829.

free-burning coals of the West Coast; it has never been equally successful with the higher-rank, better-quality—from a thermal point of view—coals of the Appalachian province. When properly operated and carefully maintained, however, the small domestic stoker is capable of remarkable performance.[38]

great enough to oxidize the coal close to the ignition level. Its coking properties are thus reduced to the point where dangerous "coke-tree" formation can be avoided. In the other, the plastic coal is forced out through a relatively narrow orifice between the top of the retort and a central "mushroom" cap, breaking up the plastic coal
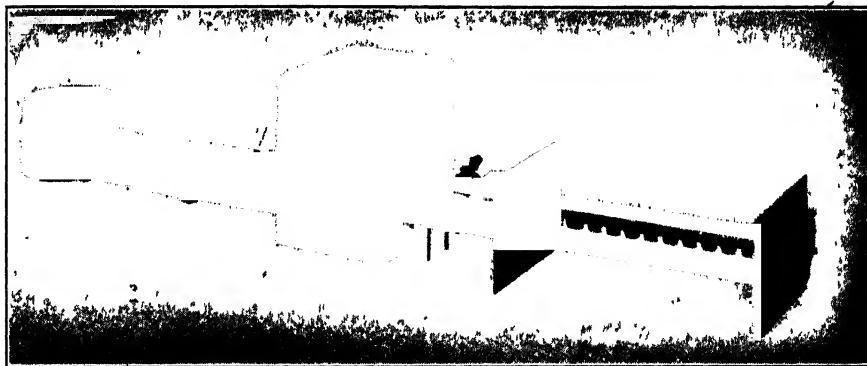
Fig. 7   Bin feed domestic stoker for 60 pounds of coal per hour.   (Courtesy of the Iron Fireman Manufacturing Company.)

The difficulties have been predominantly found in the small domestic units and have been of two types: (1) those due to the formation of "coke trees,"[39] and (2) failures to form clinker with high-ash-fusion coals. The bituminous-coal industry has financed extensive research directed at the removal of these difficulties, resulting in two designs which appear to promise success.[40]   In the first of these, air is admitted low in the retort of the stoker in amounts insufficient to support ignition but

into small, uniform pieces which are then burned on an outside grate surrounding the retort.

Still another new design for small units may be mentioned, though its relation to the underfeed stoker is merely nominal.[41] In this device coking coal is fed from a cylindrical retort toward a high-velocity air jet issuing from a nozzle, coaxial with the retort. This unit bears a similarity to the "jet" gas producer developed in Russia (see references in note 93, page 1505) and may have similar advantages which are discussed below (see references in note 94, page 1506), in addition to providing a possible method for the use of strongly coking coals. Ignition of the incoming fuel in this case is on strictly underfeed principles, as defined on page 1507, suggesting that its

38 Estep, T. G., and Saylor, D. C., *Mech. Eng.*, **56**, 547–9 (1934).   Drewry, M. K., *ibid.*, **57**, 103–9 (1935).

39 Sherman, R. A., and Kaiser, E. R., *Trans. Inst. Mining Met. Engrs.*, **130**, 388–407 (1938). Knox, W., and Doherty, J. D., *ibid.*, **149**, 254–69 (1942).

40 Guthrie, S. W., *Mech. Eng.*, **64**, 599–603 (1942).   Anon., *Bituminous Coal Research*, **2**, No. 2, 2 (1942).

41 Bailey, E. G., U. S. Pat. 2,222,756 (1940).

successful performance may depend on rather exact proportioning of the parts and that its range of ratings may be somewhat limited.

OVERFEED AND SPREADER STOKERS

Overfeed stokers of the early types, made under the names "Roney," "Murphy," "King Coal," etc., are still in fairly extensive use. Many of these units are 25 or more years old, and are still carrying the load. Such units are seldom installed new today. Descriptions of the units and of their operations are available in standard textbooks on stokers and furnaces.[42]

Spreader stokers are, however, a relatively new development, although they may be classified with overfeed stokers. They operate on the same principle as locomotive stokers, in that the fuel is projected into the furnace with considerable velocity and then falls down onto a grate through which air is drawn; they differ in that in locomotive stokers steam jets supply the propulsive force, whereas in spreaders the fuel is usually projected either mechanically, by paddles or a rapidly rotating wheel, or by the high-velocity stream of primary air by which the coal is conveyed to the burner. In locomotive stokers it is considered desirable that as much as possible of the combustion be carried out while the fuel is resting on the grate; in stationary spreader stokers a large portion of the combustion occurs in suspension, only the largest particles of the fuel reaching the grates. The principles of operation are essentially similar, so far as the fuel bed is concerned, to those obtaining in hand-firing, the stoker being merely a mechanical means of producing a continuous flow of small amounts of fresh fuel downward into it. Uniformity of air flow to all parts of the grate is secured in the spreader stoker, by using grates having relatively small air apertures, called "pinhole grates." By this means a large part of the resistance to air flow is concentrated in the grates themselves, which are always part of the fuel-bed structure; thus, the total resistance to air flow differs only slightly, whether or not there is a layer of fuel and ash on top of it. Descriptions of such units and the results of tests made on them are given by Barkley;[43] a unit of this type, with a traveling grate for ready removal of refuse, has been installed for a boiler producing 250,000 pounds of steam per hour, as shown in Fig. 8, and the manufacturers are said to be willing to provide a unit with a capacity of half a million pounds of steam per hour.

COAL SELECTION FOR STOKERS

It has already been noted that many stokers are sensitive to the characteristics of the coals supplied to them. Three characteristics of the coal are the usual sources of trouble: (1) the ash content and ash-fusion characteristics, (2) the coking characteristics of the coal, and (3) less frequently, the reactivity or ease of ignition of the coal.

Ash. Clinker trouble and slagging are probably the most frequent causes of difficulty in fuel beds. Clinkers are more or less fused masses of ash and coke which agglomerate in the fuel bed as a result of the flowing or sintering together of large quantities of partially burned fuel in hot portions of the bed. They cause trouble by interference with the normal flow of the primary air, by blocking the normal flow of fuel, especially in mechanical stokers, and

42 See, for example, Gebhardt, G. F., *Steam Power Plant Engineering*, John Wiley & Sons, New York, 6th ed., 1925, pp. 232–5.

43 Anon., *Power*, **80**, 476–7 (1936). Barkley, J. F., *Trans. Am. Soc. Mech. Engrs.*, **59**, 259–65 (1937).

Fig 8(a)   External view of spreader stoker for 250,000 pounds of steam per hour   (Courtesy of the Detroit Stoker Company)

by adhering to the supporting grates, cutting off the flow of cooling air, and thus leading to destruction of the grate structure   Slagging involves the projection of ash particles, molten or at least sticky, out of the fuel bed against furnace walls or heating surface   It causes difficulty by cutting down the heat transfer to water-cooled side walls, resulting in changes in superheat temperature, by erosion of refractory furnace walls and their ultimate destruction, and by increasing the resistance to the flow of gas through the boiler passes which may lead to decrease in the maximum rating because of limited draft

The general subject of ash and its characteristics is treated in detail elsewhere [44]

[44] Chapter 15.
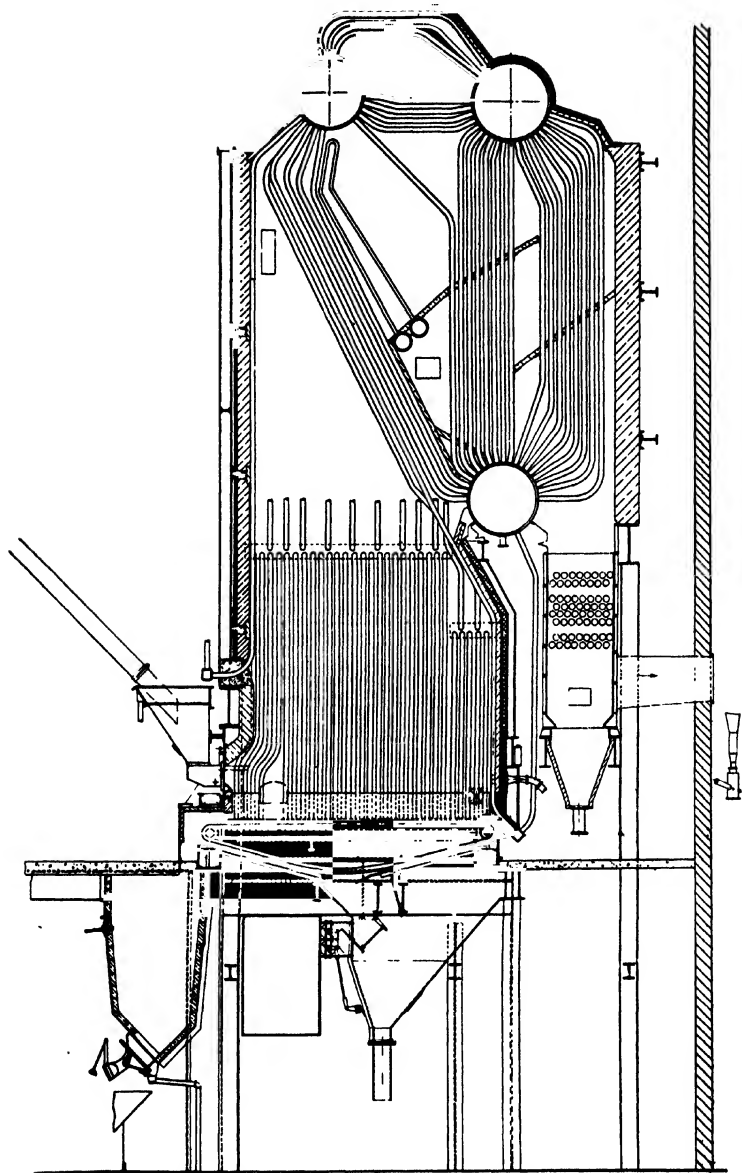
FIG. 8(b). Section showing ash-removal traveling grate for stoker of Fig. 8(a). (Courtesy of the Detroit Stoker Company.)

Relatively little is known about the mechanism of clinker formation, but there is general evidence that, other things being equal, the severity of clinker difficulty is related to the ash-softening temperature;[45] the lower the ash-softening temperature, the greater the difficulty. The rule is not exact, and many other factors may enter the picture to disturb it. In particular, the care exercised in the operation of the unit is of great importance; a given coal may cause trouble in one unit but may be quite trouble-free in a nearly identical unit answering similar demands but operated differently.

A little more is known concerning slagging difficulties, which are even more important for the operation of large pulverized-coal-fired units than they are for supported bed-fired units.[46] In a qualitative way, the conditions to be satisfied to produce slagging can be stated, and the importance of the factors of heat transfer, slag viscosity, and slag fusion temperature can be estimated. Gumz[46] has attempted to account for the fractionation of the ash constituents found along the path of gas flow in high-capacity boiler units. His success is notable only in sulfur fouling of air preheaters and other such low-temperature heating surfaces, which has been extensively investigated in this country.[47] It appears that the best preventive of slagging trouble is to limit burning rates to the point where primary air pressure is insufficient

to project burning particles against the walls or heating surfaces, or, if economic considerations make this impracticable, to assure, by adequate overfire air supply, that such particles are completely burned out and the ash residues cooled below the sticky temperature.

Coking Properties. Up to the present time there has been no generally satisfactory method of assessing the coking properties of coals, but these properties are generally agreed to be of the utmost importance for satisfactory coal performance. That this is true in a general way is evident from the ease with which free-burning coals are handled in domestic underfeed stokers, and the relative difficulty attendant on the utilization of strongly coking coals. It is quite possible, however, that the importance of this characteristic has been overemphasized. Its very unmeasurability gives it exaggerated importance so that it appears responsible for all manner of crimes. The subject of tests for coking properties of coal is treated elsewhere in this work;[48] a subcommittee of the A.S.T.M. has for several years been concerned with the selection of a test of coking properties that will be significant for combustion practice. This committee has attempted some observations of the British swelling index[48] on coals used in practice but thus far has not even been able to suggest in what way the swelling of coal may be related to furnace practice.

Smoke. One of the most serious limitations on fuel-burning capacity is imposed by the emission of objectionable smoke. An increasing awareness of the civic disadvantages of a smoke pall, and a growing desire to "do something about it" on the part of the general public,[49] have rein-

[45] Nicholls, P., and Selvig, W. A., *U. S. Bur. Mines, Bull.* **364** (1932), 71 pp.

[46] Rosin, P., and Fehling, H. R., *Ber. Reichskohlenrats,* **D52** (1933), 12 pp. Fehling, H. R., *Feuerungstech.,* **24,** 151–5 (1936) ; *J. Inst. Fuel,* **11,** 451–8 (1938). Gumz, W., *Glückauf,* **76,** 463–7, 581–6, 721–8 (1940). Gould, G. B., and Brunjes, H. L., *Trans. Am. Inst. Mining Met. Engrs.,* **139,** 364–83 (1940).

[47] Johnstone, H. F., *Univ. Ill. Eng. Expt. Sta., Circular* **20** (1929), 22 pp., *Bull.* **228** (1931), 122 pp.

[48] Chapter 6.

[49] Hood, O. P., *Mech. Eng.,* **48,** 388 (1926) ;

forced the demand for limiting the loss of efficiency due to smoke production. Strictly speaking, smoke should probably be defined as the cloud formed by airborne particles of soot and tar resulting from the incomplete combustion of fuels, but it is usual, nowadays, to broaden this meaning to include air-borne particles of any kind, including fly ash, fumes, and acid mists, emitted from a fire. This materially broadens the scope of the smoke problem since it brings into this field the emission of fly ash from powdered-coal installations, which are not guilty of incomplete combustion and which, therefore, cannot hope to improve their efficiency by smoke elimination. This poses a serious problem for large power producers [50] since the installation of equipment for cleaning flue gases is a costly procedure.[51]

Smoke, the product of incomplete combustion, appears as a limit to capacity in two different ways. In large power installations, fired by underfeed or traveling-grate stokers, smoke emission usually imposes an upper limit to maximum capacity.[25, 34] This limitation is usually associated with objectionable emission of cinder as well. It may be ameliorated by the use of overfire air under pressure as discussed above. On the other hand, smoke emission from domestic units usu-

ally occurs during periods of low rating; under these conditions [10] it cannot be eliminated by burning out in the combustion space above the fuel bed but must be prevented from forming in the fuel bed itself. Similarly, domestic underfeed stokers are likely to produce smoke during off periods, in maximum intensity at the beginning of the period, and may also offend by the ejection of fly ash during normal operation. The obvious remedy for the latter condition is the use of lower forced-draft velocities; it is the most potent argument there is for the development of a natural-draft domestic stoker.

Flue-gas-cleaning equipment of many different kinds [51, 52] is available for the removal of dusts and of acid mists, but, in general, there is no effective method of removing soot, once formed. It is desirable that more quantitative studies be made concerning the travel of smoke and dusts in normal atmospheric currents than are now available,[53] in order that the justifi-

City Manager Mag., **8**, 19–23 (June 1926). Christy, W. G., *Mech. Eng.*, **55**, 347–51 (1933). Lessing, R., *Fuel*, **15**, 221–8 (1936). Tucker, R. R., *Mech. Eng.*, **60**, 377–80 (1938). Katz, M., and Lathe, F. E., *Natl. Research Council Can. Publ.* **815** (1939), 447 pp.; *Chem. Abs.*, **34**, 5884 (1940). Burdick, L. R., and Barkley, J. F., *U. S. Bur. Mines, Inf. Circular* **7066** (1939), 14 pp.

[50] Hardie, P. H., *Mech. Eng.*, **61**, 895–6 (1939) ; discussion, *ibid.*, **62**, 557–62 (1940).

[51] Pearson, J. L., Nonhebel, G., Ulander, P. H. N., *J. Inst. Fuel*, **8**, 119–56 (1935). Anon., *Combustion*, **11**, No. 7, 37 (1940). Johnstone, H. F., and Singh, A. D., *Univ. Ill. Eng. Expt. Sta., Bull.* **324** (1940), 140 pp.

[52] Brandt, O., and Heidemann, E., *Kolloid Z.*, **75**, 129–35 (1936). Brandt, O., Freund, H., and Heidemann, E., *ibid.*, **77**, 103–15 (1936). Cawood, W., *Trans. Faraday Soc.*, **32**, 1068–73 (1936). Heinrich, K., *Combustion*, **8**, No. 8, 36–8 (1937). Rammler, E., and Breitling, K., *Feuerungstech.*, **25**, 97–104 (1937). Zimmermann, E., *ibid.*, **25**, 104–8 (1937). Wellman, F., *ibid.*, **25**, 108–16 (1937). Heinzelmann, H., *ibid.*, **25**, 116–21 (1937). Gumz, W., *ibid.*, **25**, 121–7 (1937). Heidemann, E., and Brandt, O., *Z. Ver. deut. Ing., Beiheft Folge* **1938**, No. 5, 149–52. St. Clair, H. W., *U. S. Bur. Mines, Rept. Investigations* **3400**, 51–64 (1938). Lessing, R., *Fuel*, **17**, 375–83 (1938), **18**, 21–9 (1939). Lapple, C. E., and Shepherd, C. B., *Ind. Eng. Chem.*, **32**, 605–17 (1940). Whiton, L. C., *Trans. Am. Soc. Mech. Engrs.*, **63**, 213–8 (1941). St. Clair, H. W., *Rev. Sci. Instruments*, **12**, 250–6 (1941).

[53] Bosanquet, C. H., and Pearson, J. L., *Trans. Faraday Soc.*, **32**, 1249–64 (1936). Meldau, R., *ibid.*, **32**, 1270–3 (1936). Singh, A. D., *Univ. Ill. Eng. Expt. Sta.*, *Circular* **36** (1939), 32 pp. Sherlock, R. H., and Stalker, E. A., *Mech. Eng.*, **62**, 455–8 (1940) ; *Univ. Mich., Eng. Research Bull.* **29** (1941), 49 pp.

cation for capital expenditures for flue-gas cleaning may be accurately estimated.

The proneness of a hand-fired installation to smoke depends quite strongly on the composition of the coal with which it is fired. It has been shown, in fact, that the danger of smoke is approximately proportional to the amount of tar produced by the coal in a carbonization assay test.[54]

It is evident from the discussion above that the factors entering the problem of coal selection are, at best, ill defined and cannot easily be reduced to quantitative estimation. These difficulties have led to considerable discussion among combustion engineers, starting from the elementary proposition that the least expensive coal is that which supplies most thermal energy per unit cost,[55] and leading up to the thesis that a new code is needed to govern the testing of coals for use in combustion equipment.[56] As a result, a joint committee of the American Society of Mechanical Engineers and of the American Institute of Mining and Metallurgical Engineers was formed, with the objective of formulating such codes. Models available to serve as guides include the Power Test Codes of the A.S.M.E. and codes of the Heating and Ventilating Engineers and of the British Standards Institution.[57] Tentative codes have been proposed for certain specific cases, but none has yet been approved and issued by the Joint Committee. One of the principal stumbling blocks to be overcome is the lack of precision of performance tests of steam-generating units;[58] another is the marked dependence of the performance of such units on the skill of the operators, which therefore must be assessed and standardized.[59]

The ultimate aim of such a code is to permit the choice of the most economical fuel for any given installation, account being taken of all the factors of operating and maintenance cost, the cost of supervision and testing, and fixed charges on any improvements that may be required for the fuel-burning equipment in existing installations or on the entire installation for new plants. Ultimately, such a choice may be possible on the basis of the results of laboratory-scale tests of specific objective properties of the fuel; at present, it can only be estimated from performance tests on a large number of the available fuels[60] with the attendant sources of error.[58] Evidently, much additional knowledge of the specific adaptabilities of certain fuels might be obtained from existing published data on the results of performance tests[61] if accurate descriptions of the coals

54 Rose, H. J., and Lasseter, F. P., *Heating, Piping, Air Conditioning,* **11,** 119–22 (1939). Bradbury, D. J., and Mott, R. A., *Fuel,* **20,** 100–5 (1941).

55 Randall, D. T., *U. S. Geol. Survey Bull.* 339 (1908), 27 pp. Heyn, E., and Hinrichsen, F. W., *Mitt. kgl. Materialprüfungsamt,* **28,** 168 (1910). Goldman, J. M., *Gas Age,* **33,** 175 (1914). Blake, A. F., *Ind. Eng. Chem.,* **10,** 627–9 (1918). Bement, A., *Power,* **58,** 448–50 (1923). Holaday, K. M., *Elec. World,* **84,** 863–5 (1924). Wade, C. F., *Chemistry & Industry,* **43,** 1098–100 (1924). Pirie, H. L., *Steam Engr.,* **1,** 97–9 (1931).

56 Gould, G. B., and Gibson, F. M., *Mining and Met.,* **17,** 340–3, 350 (1936). Rowan, R. L., paper presented at Joint Meeting, Fuel Div., Am. Soc. Mech. Engrs., Coal Div., Am. Inst. Mining Met. Engrs., Columbus, Ohio, October 5–7, 1939; *Mech. Eng.,* **61,** 848 (1939).

57 *Standard Code for Testing Stoker-Fired Steam Heating Boilers,* Am. Soc. Heating Ventilating Engrs., 1938, 6 pp. *Brit. Standard Code 878* (1939), 23 pp.; *J. Inst. Fuel,* **13,** 132 (1940).

58 Gould, G. B., *Combustion,* **10,** No. 11, 24–8 (1939).

59 Rode, L., *Feuerungstech.,* **24,** 135–9 (1936). Rept. of Subcommittee 2, Joint Coal Test Code Committee, January 13, 1941.

60 Tobey, J. E., *Trans. Am. Soc. Mech. Engrs.,* **60,** 17–24 (1938).

61 Schmidt, E. C., Snodgrass, J. M., and Beyer, O. S., *Univ. Ill. Eng. Expt. Sta., Bull.* 101 (1917), 101 pp. Willard, A. C., Kratz, A. P., and Day, V. S., *ibid.,* **189** (1929), 114 pp. Kratz, A. P., and Woodruff, W. J., *ibid.,* **213**

used were available. The immediate aim of the Joint Committee is to encourage the determination and reporting of such detailed descriptions in connection with extensive testing projects.

Testing large boiler units has been gradually developed [62] to a well-standardized technique.[63] A few questions still need clarification, especially with respect to the collection and reduction of samples of fuel and refuse [64] and the determination of the smaller losses, which at present are usually included in the "Unaccounted for" item; [65] these become important in connection with proposals to estimate the efficiency of small units without the expense of weighed coal tests, by subtracting the sum of all losses from 100 percent.[66]

In order to make the best use of such material, once it has been obtained for any given installation, it is essential that the results of tests be used to load steam-generating units correctly to secure maximum economy. An exact method of scheduling load has long been used for system operation in large utility power systems,[67] but it has not often been used, even there, for the scheduling of boiler units. The method consists, essentially, in adding load to that unit, or units, which produces the added increment of demand for the smallest increment of input. It is of the greatest importance, and deserves maximum consideration in systems, or boiler rooms, in which units of different ages or different economy characteristics are available.

Finally, the best choice of units to load, or to build, requires a knowledge, not merely of the fuel-firing equipment, important as that is, but of the whole system which the firing equipment is to serve. Surveys of the characteristics of power-generating equipment and of its cost are available.[68] Of great importance, in connection with this auxiliary information, are data concerning the extent and nature of the provision made for automatic control,[69] and the type of coal-handling equipment.

When all is said and done, the choice of fuel-handling and firing equipment and of fuel is a question of engineering econom-

(1930), 60 pp. McCabe, L. C., *Mining Congr. J.*, **23**, No. 12, 18–9 (1937); *Mech. Eng.*, **60**, 217–21 (1938). Coetzee, J. J., *Bull. Fuel Research Inst. (S. Africa)*, **16** (1940), 47 pp.; *Chem. Abs.*, **35**, 3794 (1941).

62 Snodgrass, J. M., *Univ. Ill. Eng. Expt. Sta.*, *Bull.* **34** (1909), 20 pp. Breckenridge, L. P., Kreisinger, H., and Ray, W. T., *U. S. Bur. Mines, Bull.* **23** (1912), 380 pp. Kratz, A. P., *Univ. Ill. Eng. Expt. Sta., Bull.* **78** (1915), 72 pp.

63 *A.S.M.E. Power Test Codes*, Am. Soc. Mech. Engrs., New York.

64 Rosin, P., Rammler, E., and Kayser, H. G., *Wärme*, **58**, 304–7 (1935). Grumell, E. S., and Dunningham, A. C., *Fuel*, **15**, 55–9 (1936). Dawe, A., and Potter, N. M., *ibid.*, **15**, 128–36 (1936). Morrow, J. B., and Proctor, C. P., *Trans. Am. Inst. Mining Met. Engrs.*, **119**, 227–76 (1936); *Fuel*, **16**, 128–47 (1937). Manning, A. B., *J. Inst. Fuel*, **11**, 153–5 (1937). *Am. Soc. Testing Materials Standard* D492-40T.

65 Haslam, R. T., *Ind. Eng. Chem.*, **15**, 679–81 (1923). Minter, C. C., *J. Soc. Chem. Ind.*, **48**, 35-8T (1929). Morgan, J. J. and Stolzenbach, C., *Gas Age-Record*, **73**, 301–4 (1934). Evans, R. N., and Davenport, J. E., *Ind. Eng. Chem., Anal. Ed.*, **7**, 174–8 (1935). Cross, B. J., *Combustion*, **7**, No. 7, 33–6 (1936). Moody, A. H., and Harrington, J. A., *ibid.*, **8**, No. 5, 33–8 (1936).

66 Anon., *Combustion*, **8**, No. 10, 21 (1937). Dulmage, W. W., *ibid.*, **8**, No. 10, 22–8 (1937).

67 Stahl, E. C. M., *Elec. World*, **95**, 434–8 (1930). Estrada, H., *ibid.*, **96**, 685–90 (1930). Lovell, A. H., *Generating Stations*, McGraw-Hill Book Co., New York, 2nd ed., 1935, pp. 168–97. St. John, E. D., *Combustion*, **8**, No. 3, 30–5 (1936).

68 Clark, F. S., *Elec. World*, **105**, 174–7 (1935). Anon., *Combustion*, **8**, No. 7, 25–32 (1937). Cross, B. J., *ibid.*, **8**, No. 6, 23–7 (1937). Rosencrants, F. H., *ibid.*, **9**, No. 10, 31–6 (1938). Clarke, C. W. E., *Trans. Am. Soc. Mech. Engrs.*, **61**, 273–90 (1939).

69 Sauermann, A., *Glückauf*, **71**, 1124–9 (1935). Keppler, P. W., *Combustion*, **8**, No. 10, 29–33 (1937). Young, J. W., and Eastwood, F. A., *J. Inst. Fuel*, **10**, 251–65 (1937).

ics; [70] it is probably generally true that, from a technical point of view, any fuel can be burned on any equipment provided that sufficient care is taken in maintenance and operation. Whether the job shall be done one way or another is not usually a question of technological practicability but of how the cost of producing useful heat can be minimized. Finally, the most important single property that the fuel should have for such economical operation is uniformity,[71] since such analyses as those outlined cannot be repeated frequently to accommodate frequent changes in the fuel characteristics. Uniformity of fuel from car to car, from day to day, month to month, and year to year makes for the maximum satisfaction in any heating project.

THE PHYSICS OF COMBUSTION

From the physical point of view, all the processes discussed above have three characteristics in common. In all of them, fuel, in the form of a bed of broken solids, is supported on a grate, and air to support combustion is blown through the bed. A portion of the heat released is returned to incoming fuel, by mechanisms which are different in the different types of equipment, to heat it to the temperature at which combustion becomes self-supporting. Finally, the remainder of the heat is distributed between losses from the bed directly to its supporting structure or to the furnace enclosure and sensible heat in the gases of combustion.

It is, at once, obvious that the mechanisms which determine this distribution must be physical since they deal with the convection, conduction, and radiation of heat, with temperature gradients, and with gas flow. The mechanism which governs the rate of release of energy in the form of heat is also dominantly physical; it depends mainly on the geometry of the fuel bed and on such physical characteristics as the magnitude and shape of the voids between particles of the bed and the properties of the fluid flowing through the voids. These condition the speeds of the chemical processes occurring at the interface between gas and the solid materials of the bed to such an extent that, from an analytical point of view, the chemical reactions supply only one of several sets of boundary conditions to a system defined by the physical properties of the fuel bed.

COMBUSTION RATES REFERRED TO UNIT SURFACE OF FUEL

Early chemical investigations of the combustion reactions were devoted to attempts to determine the rate of the chemical reactions and to choose between the two oxides as primary products, as shown in the next section of this report, but they served to indicate that no such investigation could be considered representative of conditions in fuel beds because, in order to secure reaction rates that were small enough to measure, the reactions had to be controlled at temperatures several hundred degrees below those prevailing in real beds; at fuel-bed temperatures the rates became too fast for the methods of measurement available. It was soon recognized,[72] however, that only exceptionally did the rate of the

[70] Schiefer, H. V., *Power*, **77**, 628–9 (1933). Harkins, H. D., *Trans. Am. Soc. Mech. Engrs.*, **57**, 11–34 (1935). Peacock, H. M., *J. Inst. Fuel*, **11**, 230–9 (1938). Webber, A. F., *Iron Steel Ind.*, **11**, 264–6 (1938). Anbro, G. A., *Mech. Eng.*, **61**, 804–6 (1939); discussion, **62**, 555–7 (1940). Daniels, G. C., *Mech. Eng.*, **63**, 801–6 (1941).

[71] Randall, D. T., in ref. **55**. Dunningham, A. C., *Colliery Guardian*, **144**, 455–7 (1932). Holmes, C. W. H., *Coke Smokeless-Fuel Age*, **2**, 161–2, 203–4, 226–8, 249–50 (1940).

[72] Nusselt, W., *Z. Ver. deut. Ing.*, **68**, 124–8 (1924). Rosin, P., *Braunkohle*, **24**, 241–59 (1925). Ward, J. T., and Hamblen, J. B., *Ind. Eng. Chem.*, **19**, 1025–7 (1927).

heterogeneous reaction between the fuel and the air for combustion limit the rate of burning at fuel-bed temperatures; in general, the speed of combustion was limited by the rate at which oxygen could be transported to the immediate neighborhood of the reacting surface. Thus, the study of combustion rates became a study of the rate of the transport processes required to maintain a concentration of the reacting gas at the solid surface.

Experimental work in this field was stimulated by the development of powdered-coal firing of large power boilers in the 1920's,[73] but the methods used were more easily adapted to the study of large particles, so the investigations soon turned to material of direct interest in grate firing. Direct measurements of the rate of oxidation of solid materials have been carried out by the suspension of spheres of graphite, usually nearly ash-free, in a regulated stream of air or other oxygen-nitrogen mixture in a furnace whose temperature could be controlled. Provision was made for weighing the carbon particles, either intermittently[74] or continuously.[75] This work showed that the rate of the specific surface reaction depended strongly on the temperature at low temperatures[75] but less so at high ones;[74, 75] that it was directly proportional to the oxygen concentration in the gas flowing over the carbon surface;[75] that it depended on approximately the 0.4 power of the mass velocity of the gas at high temperatures;[74, 75] and that, for small particles, it was approximately inversely proportional to the diameter of the particle.[74]

These results accord with a mechanism in which the high rate of the surface reac-

tion reduces the concentration of oxygen at the particle surface to such an extent that the speed of the process is limited by the rate of transport of oxygen to the surface, and thus are in agreement with earlier hypotheses.[72] Similar effects were found for the reduction of carbon dioxide and steam,[76] in work in which the monotonic effect of increasing gas velocity was used to estimate the absolute reaction rate by increasing the gas flow until no further increase in reaction rate, as measured by gas analysis, was found.

The first analyses of the transport process were based on the hypothesis that diffusion was responsible for moving oxygen from the body of the gas to the reaction surface.[72] A pure diffusion process could not, however, account for the dependence of the observed reaction rates on the gas velocity, so the concept of the existence of a stagnant film of a thickness dependent on the flow velocity[75, 77] was borrowed from the early work on convective heat transfer to account for this effect. This concept stimulated work in which the diffusion constants for oxygen and carbon dioxide in mixtures with nitrogen were determined in apparatus in which a fixed path was set up between the flowing stream and the reacting surface,[78] and in which the gas composition was determined, by microsampling technique, by direct analysis at various points in the neighborhood of a burning spherical carbon surface.[79] The improved diffusion coefficient from this work permits a close correlation of the experimental re-

73 Chapter 34.

74 Smith, D. F., and Gudmundsen, A., *Ind. Eng. Chem.*, **23**, 277–85 (1931).

75 Tu, C. M., Davis, H., and Hottel, H. C., *ibid.*, **26**, 749–57 (1934).

76 Mayers, M. A., *J. Am. Chem. Soc.*, **56**, 70–6, 1879–81 (1934); **61**, 2053–8 (1939).

77 Burke, S. P., and Schumann, T. E. W., *Ind. Eng. Chem.*, **23**, 406–12 (1931); *Proc. 3rd Intern. Conf. Bituminous Coal*, **2**, 485–509 (1931); *Ind. Eng. Chem.*, **24**, 451–3 (1932).

78 Davis, H., and Hottel, H. C., *Ind. Eng. Chem.*, **26**, 889–93 (1934).

79 Parker, A. S., and Hottel, H. C., *ibid.*, **28**, 1334–41 (1936).

sults obtained by Hottel and his collaborators by the use of the bounded-film concept mentioned above. This ·work also results in several other conclusions which will be of interest in a later section of this report: (1) that carbon dioxide, only, but no carbon monoxide was found in the neighborhood of the carbon surface, and (2) that the rate of reaction, referred to the concentration of oxygen at the carbon surface so that the true heterogeneous reaction rate is calculated, varies with temperature according to the Arrhenius equation, as is to be expected, the heat of activation being 44 kilocalories.

This correlation fails, however, to account for the rates of burning observed on smaller particles,[74] giving results about 40 percent too low. This appears to be the direct result of the film concept, since it leads the authors to estimate the transport of oxygen through the film as the sum of two contributions, one due to simple diffusion in an unbounded, quiescent gas, and one due to transport through a bounded film. The latter is large for large particles and high velocities, by comparison with the former; its dependence on particle size arises from an argument by analogy resulting in the dependence of film thickness on Reynolds' number. This dependence was determined experimentally, however, only from the dependence of the rate of burning on the mass velocity of the gas, indicating that the film thickness is proportional to the 0.37 power of the gas velocity, hence of the Reynolds number and, hence, of the particle diameter.

However, as noted above, the dependence of the burning rate on the particle diameter is very nearly one of inverse proportion,[80] which is the dependence due to simple diffusion in an unbounded film.

Evidently, then, the contribution due to transport through the bounded film in Hottel's correlation does not change over to the form corresponding to simple diffusion at a large enough value of particle radius. It is to be noted, moreover, that the micro-sampling investigation showed no marked change in the concentration gradients with distance from the particle, as would be expected according to the bounded-film concept. These difficulties can probably best be met by a complete abandonment of the film idea, as has been found necessary in heat-transfer work, and the adoption of a more sophisticated notion of the Reynolds analogy [81] in which the whole mass transfer coefficient is made to depend on the Reynolds number and the mass transfer equivalent of the Prandtl number. An adequate treatment of this subject would probably have to start from the basic equations of combined convection and diffusion,[80, 82] and would serve not only to iron out the discrepancies noted above but might also permit the exact interpretation of the model experiments [83] made by Rosin and his associates.

COMBUSTION RATES IN FUEL BEDS

At first glance, it seems relatively simple to extend these results of measurements of burning rate per unit surface to a unit volume of a bed of broken solids by multiplying the reaction rate per unit surface by the specific surface of the bed. Investigations of the flow of fluids through such

[80] Mayers, M. A., *Chem. Revs.*, **14**, 31–53 (1934).

[81] Chilton, T. H., and Colburn, A. P., *Ind. Eng. Chem.*, **26**, 1183–7 (1934). Sherwood, T. K., *ibid.*, **36**, 817–40 (1940).

[82] Förster, T., and Geib, K. H., *Ann. Physik*, **20**, 250–60 (1934). Damköhler, G., *Z. Elektrochem.*, **42**, 846–62 (1936); **43**, 1–8, 8–13 (1937). Frank-Kaminetskii, D. A., *Acta Physicochim. U.R.S.S.*, **12**, 9–12 (1940); *Chem. Abs.*, **34**, 5728.

[83] Rosin, P., and Kayser, H. G., *Z. Ver. deut. Ing.*, **75**, 849–57 (1931).

beds,[84] however, indicate that so simple a a picture cannot represent the facts. The specific reaction rate is a function of the flow velocity; but in a porous bed the velocity varies from point to point and is, apparently, not even constant with respect to its state of turbulence. The correlations referred to above have been obtained for the resistance to flow of a bed,[85, 86] but many of the published data have not been correlated according to the relations there developed. Furthermore, a bed of broken solids, while lacking the sharply defined critical value for transition from viscous to turbulent flow found in pipes, has another one not found in such simple systems, namely, the point at which the pressure drop due to friction loss through the bed becomes equal to the density of the bed, causing its disruption.[87]

In flow through pipes and ducts, the correlation of heat-transfer coefficients with fluid turbulence has preceded and guided the correlation of mass-transfer coefficients, but in the study of beds of solids there are as yet only two investigations of heat transfer,[88] and in the last of these the data were not even interpreted to obtain the heat-transfer coefficients. Thus, there is no guide from the heat-transfer work as to how the coefficient in a bed of solids is related to the unit surface coefficient; hence, transfer coefficients, or burning rates, and their dependence on gas velocity, temperature, and particle size or specific surface, cannot now be estimated from the measurements of specific reaction rate; they can be determined only by analysis of the measurements made in beds of burning fuel.

Different types of fuel beds differ in the means provided for heating and igniting the entering fuel, but, eventually, all of them provide a bed of discrete particles of carbonized fuel, heated to incandescence, into which the air for combustion is introduced. The work described above, on specific burning rates, suggests that the rate of consumption of the reacting gases, oxygen and carbon dioxide (also water vapor, where present), would be nearly independent of the temperature, above some lower limit, and that they would be of the first order with respect to the reacting gas concentrations. If this were true, the variation of gas analysis along the path of air flow with penetration into the fuel bed could be calculated on the assumption of constant first-order reaction rates, which, for constant mass velocity, leads to the exponential dependence of oxygen, or carbon dioxide, concentration on distance from the point of admission.[89, 90] Thus, the values of μ_1/G, where μ_1 is the overall rate of consumption of oxygen per unit oxygen

[84] Kozeny, I. J., *Sitzber. Akad. Wiss. Wien,* **137,** Abt. IIa (1928). Muskat, M., and Botset, H. G., *Physics,* **1,** 27–47 (1931). Carman, P. C., *Trans. Inst. Chem. Engrs. (London),* **15,** 150–66 (1937). Ward, W. H., *Engineering,* **148,** 435–8 (1939). Fowler, J. L., and Hertel, K. L., *J. Applied Phys.,* **11,** 496–502 (1940).

[85] Furnas, C. C., *U. S. Bur. Mines, Bull.* **307** (1929), 144 pp. Arend, W., *Ber. Reichkohlenrats,* **D53** (1933), 66 pp.; *Arch. Wärmewirt.,* **14,** 132 (1933). Diepschlag, E., *Feuerungstech.,* **23,** 133–6 (1935). Dunningham, A. C., and Grumell, E. S., *J. Inst. Fuel,* **9,** 24–9 (1935). Arbatsky, I., *Feuerungstech.,* **25,** 233–5 (1937). Fehling, H. R., *ibid.,* **27,** 33–44 (1939).

[86] Bennett, J. G., and Brown, R. L., *J. Inst. Fuel,* **13,** 232–46 (1940); *Gas J.,* **232,** 378, 333–6 (1940).

[87] Hirst, A. A., *Trans. Inst. Mining Engrs. (London),* **79,** 463–97 (1930), **85,** 236–71 (1932–3), **94,** 93–113 (1937–8). Arend, W., in ref. 85.

[88] Furnas, C. C., *Ind. Eng. Chem.,* **22,** 26–31, 721–31 (1930); *Trans. Am. Inst. Chem. Engrs.,* **24,** 142–86 (1930); *U. S. Bur. Mines, Bull.* **361**

(1932), 88 pp. Saunders, O. A., and Ford, H., *J. Iron Steel Inst. (London),* **141,** 291-316P (1940).

[89] Furnas, C. C., *Ind. Eng. Chem.,* **28,** 498–502 (1936).

[90] Mayers, M. A., *Trans. Am. Soc. Mech. Engrs.,* **59,** 279–88 (1937); *Fuel,* **21,** 4–11 (1942).

partial pressure per unit volume of the bed, and G is the mass rate of flow of gas along the path under consideration, and of μ_2/G, where μ_2 refers to the rate of consumption of carbon dioxide, can be estimated from observations of gas analysis at various levels in a fuel bed, simply by plotting the oxygen, or carbon dioxide, concentrations on semi-logarithmic paper against distance from the point of injection and determining the slope of the resulting line. It should be noticed that this correlation makes no assumptions, for the reaction with oxygen, concerning the nature of the primary reaction or its products, except that, on the whole, it must be of the first order.

Estimates of such reaction rates have been made [89, 90, 91] from the measurements reported before 1940.[92] Except for the work of Kreisinger, Augustine, and Ovitz, all these measurements were made on beds of coke, usually in commercial sizes. Of the Kreisinger data, only those made on coke are sufficiently regular to permit estimation of the values of the parameters under discussion. All these observations were made on intermittently fired overfeed beds. In these beds the entering air was exposed to the residue from fuel which had been partly consumed during its passage through the bed, and whose size and condition, as shape, ash content, and reactivity, might

have been quite variable. Hence, the values of the reaction rates near the point of air admission to such beds could be quite variable. From this point of view, it is unfortunate that all the observations on which estimates of these quantities have been based have been made on this type of bed, but the difficulty has been minimized by the experimental procedure, which has almost always included very thorough cleaning of the fire before fuel-bed gas samples were taken. For coke sized between 1- and 1.5-inch screens, the apparent rate of consumption of oxygen was given by Mayers and Landau [91] as:

$$\mu_1 = 183G^{0.5} \tag{1}$$

where μ_1 is given in pounds of oxygen consumed per cubic foot of bed per hour, per atmosphere partial pressure of oxygen, and G is in pounds of air flowing per square foot of bed cross section per hour. Estimates of the dependence of this rate on the particle size of the bed and on its density of packing were given in Mayers' 1942 paper.[90] The exponent 0.5 is not to be interpreted as in disagreement with the work on specific reaction rates; [74, 75, 78, 79] the precision of the data does not permit a closer estimate of this quantity.

Measurements by Chukhanov and Karzhavina [93] were used by the authors to support a hypothesis concerning the nature of the primary reaction, in accordance with which they set up their measurements as the sum of two reactions, one of them being of zero order with respect to oxygen

91 Mayers, M. A., *Trans. Am. Inst. Mining Met. Engrs.*, **130**, 408–24 (1938). Mayers, M. A., and Landau, H. G., *Ind. Eng. Chem.*, **32**, 563–8 (1940).

92 Kreisinger, H., Augustine, C. E., and Ovitz, F. K., *U. S. Bur. Mines, Tech. Paper* **137** (1916), 76 pp. Perrott, G. St. J., and Kinney, S. P., *Trans. Am. Inst. Mining Met. Engrs.*, **69**, 543–84 (1923). Sherman, R. A., and Blizard, J., *ibid.*, **69**, 526–42 (1923). Sherman, R. A., and Kinney, S. P., *Fuel*, **5**, 98–105 (1926). Nicholls, P., Brewer, G. S., and Taylor, E., *Proc. Am. Gas Assoc.*, **8**, 1129–43 (1926). Nicholls, P., *ibid.*, **10**, 1127–36 (1928). Mott, R. A., and Wheeler, R. V., *The Quality of Coke*, Chapman & Hall, London, 1939, p. 144.

93 Karzhavina, N. A., *J. Tech. Phys. (U.S. S.R.)*, **8**, 725–36 (1938); *Tech. Phys. (U.S. S.R.)*, **5**, 633 (1938); *Fuel*, **19**, 220–5 (1940). Chukhanov, Z. F., and Karzhavina, N. A., *J. Tech. Phys. (U.S.S.R.)*, **9**, 1932–44 (1939); *Fuel*, **20**, 44–7, 73–7 (1941); *J. Tech. Phys. (U.S.S.R.)*, **10**, 1256–67 (1940); *Fuel*, **20**, 186–94 (1941). Cf. also Frank-Kamenetskiĭ, D. A., *J. Tech. Phys. (U.S.S.R.)*, **9**, 1457–64 (1939); *Chem. Abs.*, **34**, 1836 (1940).

concentration, and the other of higher order than the first and approaching second order. Their data, however, when plotted on semi-logarithmic coordinates as discussed above, yield straight lines, as shown in Fig. 9. This suggests that their complex reaction is not necessary to account for the observed reaction rate, though it might be helpful in predicting the nature of the products, and indicates that these measurements may not be at variance with the earlier data.[92] However, the resulting coefficients have not yet been compared with those previously correlated.[89, 90, 91] Such a comparison will be valuable since the Russian measurements apply to a different range of sizes and of gas velocities than the older ones.

Thring and Nicholls[94] observed the carbon dioxide concentrations in the portions of a deep fuel bed where the oxygen had been entirely consumed, and they calculated the rate of the first-order reaction of consumption of carbon dioxide. Their results confirm the first-order dependence of this reaction on carbon dioxide concentration and permit an estimate of its dependence on temperature since their method of correlation does not depend on the assumption that the reaction rate is constant. This precaution is probably essential in the consideration of the rate of the reduction reaction because the heterogeneous chemical reaction is, in this case, much slower than that of consumption of oxygen. Hence, it is probable that the reaction velocity is only partly determined by the conditions of mass transfer. In support of this view, Thring found that the temperature coefficient of f_1, his nomenclature for the rate of the reduction reaction which corresponds to μ_2/G used above, led to an increase of

the rate of 50 to 100 percent for an increase in temperature of 100° C. Exact measurements of the rate of this reaction
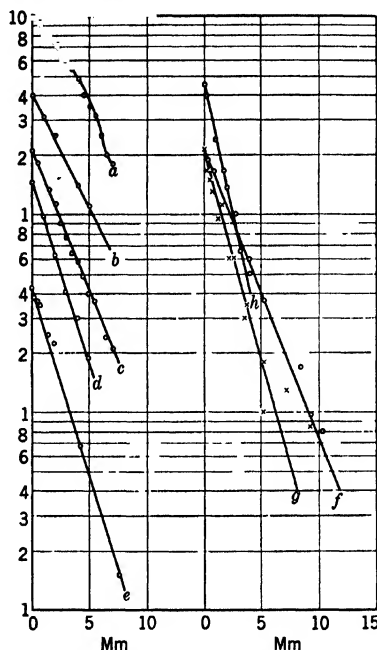
FIG. 9. Data of Chukhanov and Karzhavina to semi-logarithmic coordinates. Fuel-bed gas analyses plotted to semi-logarithmic coordinates. Data from reference 93.

CURVE	OXYGEN CONCENTRATION AT 0 M M. PERCENT	AUTHORS	AUTHORS' FIG. NOS.
a	10	Chukhanov and Karzhavina	9
b	40	"	13
c	21	"	11
d	14.5	"	10
e	42	"	12
f *	21	Karzhavina	6
g †	21	"	7
h ‡	42	"	8

* Gas velocity, 0.81 meter per second.

†Gas velocity, 0.81 meter per second; layer of fireclay under char.

‡ Gas velocity, 0.69 meter per second; distance scale halved.

94 Thring, M. W., *J. Inst. Fuel*, **14**, 47–62 (1940). Nicholls, L. H. F., *ibid.*, **14**, 71–3 (1940); *Gas J.*, **233**, 109–10, 115 (1941).

lead to a heat of activation of about 50 kilocalories[76] and so to a doubling of the reaction rate every 40 degrees. The discrepancy may easily be accounted for on the ground that a portion of the resistance to reaction is chemical, with a high temperature coefficient, and a portion is associated with the transport phenomenon and has a low temperature coefficient. It is evident that it is very difficult to estimate effective reaction rates from any data but those taken under exactly the conditions of interest.

It is evident that the state of our knowledge of the rates of these important reactions under the conditions prevailing in technical applications is still woefully small. Marked improvements in application may, quite possibly, await increases in this knowledge; the work of Chukhanov mentioned above,[93] is already being applied in the development of new types of gas producers.

HEAT FLOW IN FUEL BEDS

Although the reaction rates discussed above are of the utmost importance in determining the rate of heat release within the fuel bed, a complete knowledge of them, or of their integrals, the extent to which the reactions have proceeded at any point, does not account for the temperatures observed.[95] Heat released by the combustion reactions not only serves to heat the combustion gases and the fuel but also is transmitted through the bed to its supporting structure, to the furnace above it, and to external wall losses. The flow of heat between adjacent particles probably occurs largely by way of radiation processes, at least in the high-temperature re-

gion, but the fuel bed, as a whole, appears to have a property akin to thermal conductivity in that heat flows along temperature gradients from regions of high temperature to those of lower temperature.

According to this point of view, the temperature at any point in a fuel bed is the resultant of the total heat released along the path of air flow from admission to the point under consideration, corrected for the amount of heat, which may be quite considerable, conducted away. Depending on its position in the bed, this heat may have been conducted into incoming fuel, thus supplying the heat for ignition, or to the grate; it may have been conducted to the furnace walls and so lost; or it may have been converted to useful heat in the product. Thus, the temperature at any point represents a balance among three processes: (1) the combustion processes releasing heat, (2) the transport of heat by convection, either by gases or by solid materials of the fuel bed, and (3) the conduction of heat along temperature gradients. These processes may be given mathematical expression for simple types of fuel bed, and it has been shown that the solution of these expressions successfully reproduces the rates of ignition observed in pure underfeed burning.[90, 91]

At this point, the geometry of different types of fuel beds becomes of considerable interest. P. Nicholls[95] is responsible for a classification of fuel beds into three primary classes: underfeed, in which the flow of air and of fuel, in a bed that continuously reproduces itself, are in the same direction; overfeed, in which the flows of air and of fuel are in opposite directions; and crossfeed, in which the flows of fuel are at right angles. The first two of these classifications are essentially the same as the classifications of parallel and counterflow used to describe heat exchangers and chem-

[95] Nicholls, P., and Eilers, M. G., *Trans. Am. Soc. Mech. Engrs.*, **56**, 321-6 (1933). Nicholls, P., *U. S. Bur. Mines, Bull.* **378** (1934), 76 pp., especially pp. 9-11.

ical processing plant, but there is no satisfactory analog to crossfeed. Underfeed burning is not perfectly exemplified in any conventional burning equipment, according to Nicholls, although it will appear that it is very closely approximated by the bed of a traveling-grate stoker; overfeed burning is represented by hand-firing, to a certain extent by spreader stoker fuel beds, and by gas producers and blast furnaces. Crossfeed burning, which, according to Nicholls, is exemplified by traveling-grate fires, is better represented by underfeed stoker beds, both single- and multiple-retort types.

From the present point of view, the overfeed fuel bed is characterized by the fact that fresh fuel entering is exposed to heat supplied by gas flowing out of the fuel bed, usually at a very high temperature, and containing little or no oxygen but often products of incomplete combustion. The actual temperature of the gas to which raw fuel is exposed depends on whether the bed is operated for the purpose of generating heat for steam or process, as in a hand-fired boiler or domestic heater, or for the purpose of heating the material of which the bed is composed, as in a gas producer or blast furnace. In producers and blast furnaces, the temperature may be, and for high thermal efficiency should be, quite low, since heat in the gas is of no value once it leaves the bed. When the bed is operated to heat the materials of which it is composed, the rate at which the temperature falls, at least beyond the point where rapid reactions are occurring, depends almost entirely on the ratio $\rho U/Gc$, where ρ is the heat capacity of the solid material, U its rate of flow, G the rate of flow of gas, and c its heat capacity.[90, 96] Where, however, the bed is operated for producing heat for external use, ρU is usually not more than

about 10 percent of Gc, so that only a small portion of the heat developed in the bed is needed to prepare the incoming fuel, and the gases may contain almost all the heat developed during the combustion process. When this is so, there is practically no limit to the rate at which fuel can be ignited by gas convection.

Although the available analysis probably applies to overfeed fuel beds in the steady state,[90] these are generally characterized by intermittent firing with the special exception of spreader and locomotive stokers. With intermittent firing, a pseudo steady state may be set up between firings, when all the fresh fuel has been ignited; this is the condition in which temperatures and gas analyses have usually been measured.[92] Little information is available that takes into account the downward flow of material in the overfeed bed with the exception of gas producers[97] and of blast furnaces,[98] and only in Thring's work has there been any attempt to fit these data by the results of analysis.

Thring[94] accepted the principle that the temperature at any point in the bed is the resultant of the heat release between the point of air admission and the point under consideration, diminished or augmented by the heat conducted or convected to or away from the point. However, as he did not make the simplifying assumption that conduction at right angles to the path of flow of the gas can be neglected, he was unable to integrate the expression for temperature. It is apparent from his analysis of L. H. F. Nicholls' experimental data that such an assumption would be greatly in error for these conditions; that making

96 Mayers, M. A., *Blast Furnace Steel Plant*, **29**, 705-9 (1941).

97 Horak, W., *Z. österr. Ver. Gas- u. Wasserfach.*, **73**, 170-81, 194-203 (1933). Müller, W. J., and Graf, E., *Brennstoff-Chem.*, **20**, 241-6 (1939). Lepsoe, R., *Ind. Eng. Chem.*, **32**, 910-8 (1940). See also Chapter 37.

98 Chapter 24.

it would, in fact, negate the possibility of explaining the experimental results. The differences which occur with different arrangements of air inlet and with fuels having different properties depend on the extent to which they permit heat loss by conduction to the sides of the fuel bed from the zone of rapid reaction. The more completely such losses are inhibited, the higher the temperature in that zone, and the higher the quality, in terms of increased heating value, of the gas obtainable from the unit. In fact, Thring was able to suggest an explanation for the results of Karzhavina and Chukhanov,[93] that does not require the assumption of a special reaction mechanism since the arrangements used for securing increased gas velocity by the Russian investigators are just those required to reduce the proportional heat loss from the zone of active burning. The increased rate of formation of carbon monoxide may be explained by the increased rate of reduction of carbon dioxide associated with the higher temperature. This may also be the explanation of the apparently greater value of μ_2 required [91] to explain the high rate of formation of carbon monoxide in the lower parts of some beds, although it may also be due to the failure of carbon monoxide, produced in the primary surface reaction, to be oxidized during its diffusion away from the carbon surface.

In underfeed burning, on the other hand, the flow of fuel is in the same direction as that of the air, so that the advance of the zone of ignition is in the opposite direction to that of the air flow. Under these circumstances, convection of heat, far from assisting in the ignition of the incoming fuel, tends to prevent it by removing heat conducted into the raw fuel and carrying it back into the hotter part of the bed. Thus, the rate of ignition is limited by the rate at which heat can be conducted into the

fresh fuel, a relatively slow process; it is zero for some small value of air rate below which the rate of heat release by the combustion reaction is only great enough to compensate for losses and thus cannot produce heat flow into incoming fuel.[91] This is the condition that is measured experimentally in such tests as the critical air blast.[98] As the air-flow rate increases above this lower limit, the rate of ignition increases faster than the rate of burning [90, 95] because of the increase in μ_1 and the initial decrease in the solid-gas heat-transfer coefficient with air-flow rate, without a concomitant increase in the conductivity of the bed. As the flow rate increases further, however, the convection of heat back into the burning zone from the entering fuel through which the air passes first increases to such an extent that it overtakes the increasing rate of conduction and sets an absolute upper limit on the rate at which fuel may be ignited. Beyond this maximum, the rate of ignition falls off continuously with increasing air flow and, with some fuels, may reach zero again at a high rate of air flow.

Investigation has shown that the fuel beds of traveling-grate stokers approximate very closely to the conditions of underfeed burning [26]—to such an extent, indeed, that experimental methods similar to P. Nicholls' [95] have been used to predict traveling-grate performance.[99] This comes about because the velocity of grate travel is so great by comparison with the rate of travel of the ignition zone that planes parallel to this zone have a negligible projection on

[99] Tanner, E., *Veröffentl. Ver. Kraftwirts. Ruhrzechen*, **1934-5**, No. 1, 40 pp. Rosin, P., Kayser, H. G., and Fehling, H. R., *Ber. Reichskohlenrats*, **D51** (1935), 61 pp. Rosin, P., and Fehling, H. R., *J. Inst. Fuel*, **11**, 102–17 (1937). Dunningham, A. C., and Grumell, E. S., ref. 85; *J. Inst. Fuel*, **11**, 117–22, 129–33 (1937), **12**, 87–95 (1938); *Fuel*, **17**, 324–7 (1938).

the vertical axis, and, hence, only negligible amounts of heat are conducted along the axis parallel to the grate travel. Under these conditions, the direction of grate travel can be taken as equivalent to a time coordinate, and conduction in this direction can be neglected. Hence, the analysis referred to [90] may be immediately applied to beds of free-burning, nonswelling fuels when fired in such equipment. Insufficient data are now available for the analysis of conditions in beds of coking fuel, although results with such fuels have been described by Tanner and by Dunningham and Grumell.[99]

The typical device in which crossfeed of the fuel is the dominant mode of ignition is the underfeed stoker.[29, 35] In this device the flow of heat into the fuel takes place principally across a nearly vertical plane extending lengthwise of the stoker between the center line of each retort and that of the next adjacent tuyère stack. Although this description applies strictly only to the multiple-retort type, it is easily extended to the single-retort type [100] by consideration of obvious differences in geometry. This system has not been subjected to analysis because of the mathemaical difficulties inherent in a two-dimensional problem, athough an attempt is being made to circumvent the mathematical difficulties [101] by the use of an electrical analog, an electrical integrator for the partial differential equations of heat flow under consideration.

The air for combustion in the underfeed stoker does not pass through the fuel entering the bed. Thus, the conditions leading to ignition of fresh fuel are quite different from those in either underfeed or overfeed burning since convection does not enter the picture. In an underfeed stoker, the fuel entering the zone of active combustion is heated from the side, in a system geometrically similar to that of a by-product coke oven, in that heat flows, probably by conduction, from a heated face through a section of already heated coke into raw coal,[29] as shown in Fig. 10. The differential equation governing this system has been stated,[102] although the boundary conditions obtaining there probably should be modified as follows. The hot face of the coke, instead of instantaneously rising to the final temperature, and thereafter being maintained at that level, should probably be represented as being instantaneously subjected to heat transfer from a source at constant temperature. This change in the boundary condition results in characteristic solutions to the equation determined by eigenvalues [103] which are the solutions to the equation:

$$\tan \lambda_n = \frac{\alpha l}{k \lambda_n}$$

where the λ_n are the eigenvalues, α is the heat-transfer coefficient, k is the thermal conductivity, and l is the half-length of the thermal path. With this result, reasonable choice of the values of α and k results in a variation of heating time in proportion to the 1.6 power of the retort width, in accordance with experience in practice.[104]

The remainder of the scheme of the underfeed stoker may be taken as an example of overfeed burning above the tuyères. In the analysis of all such beds,

[100] Barnes, A. C., *Bituminous Coal Research, Inc., Tech. Rept.* **4** (1938), 69 pp.
[101] Work in progress, Coal Research Laboratory. Cf., Beuken, C. L., *Feuerungstech.*, **26**, 7-9 (1938). Avrami, M., and Little, J. B., *J. Applied Phys.*, **13**, 255-64 (1942).
[102] Burke, S. P., Schumann, T. E. W., and Parry, V. F., *Proc. Am. Gas Assoc.*, **1930**, 820-55.
[103] Von Mises, R., *Riemann-Weber Differentialgleichungen der Physik*, F. Vieweg & Son, Braunschweig, 1925, pp. 264-79.
[104] Lowry, H. H., Landau, H. G., and Naugle, L., *Trans. Am. Inst. Mining Met. Engrs.*, **149**, 297-330 (1942). See also Chapter 22.
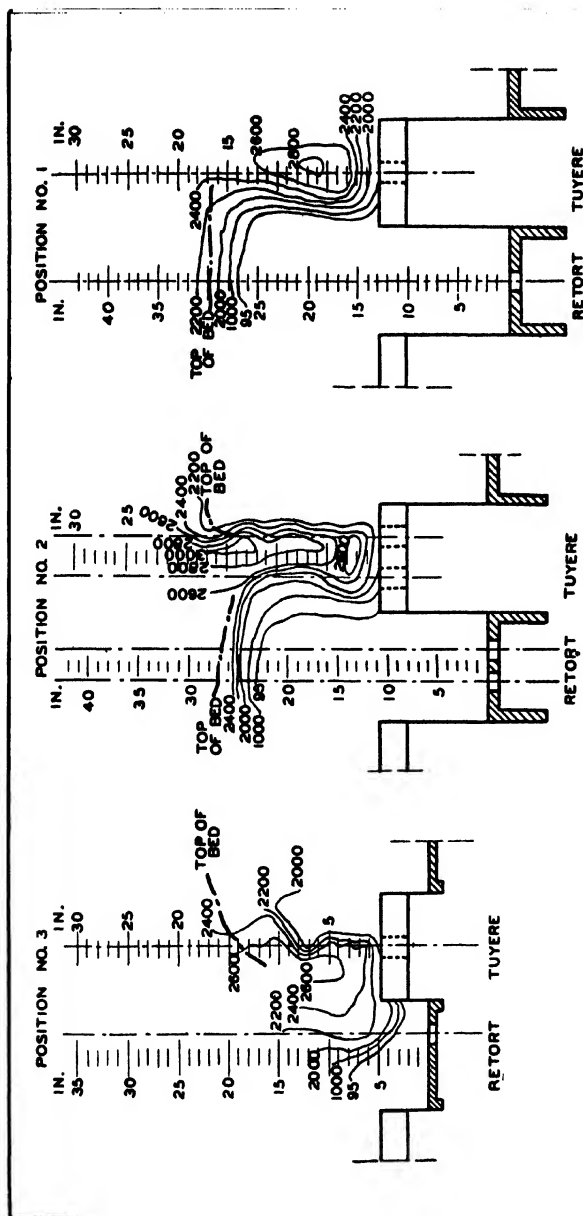
Fig. 10. Temperature contours in a cross section of a multiple-retort stoker fuel bed. Mayers and coworkers.[19]

Position 1, 1 foot 4 inches from front wall.
Position 2, 4 feet 0 inch from front wall.
Position 3, 8 feet 2½ inches from front wall.

Dot and dash lines represent openings for insertion of measuring probes.

the path of flow of the gas is of fundamental importance, but it is rarely regular enough to justify calculations with a constant, uniform mass flow rate. In the underfeed stoker the flow probably follows a relatively tortuous path whose cross-sectional area is not simply related to the stoker structure but depends in a complicated way on the mechanical adjustment of the equipment, the properties of the fuel, and the rate of burning; in equipment whose air inlets are nozzles, as in some gas producers and in blast furnaces, it may, with present knowledge, be almost impossible to define the path.

Bennett and Brown [86] have made a start at determining these conditions by the method of model testing; their results have been supplemented, to some extent, by measurements of air-flow distribution in unignited fuel beds.[105] It is possible that the differential equations describing the fuel bed can be integrated in terms of a coordinate system based on the flow lines if they can be predetermined, but no attempt to do this has yet been observed. One of the difficulties in such a procedure would be the description of flow paths; but it is believed that simplifying assumptions for a bed of broken solids may be made on the basis of a statistically average element of volume of the bed. For such an average, it will be necessary to have better knowledge than is now available of the average mode of packing of a bed, its average void volume and effective pore diameter, and the dependence of these properties on the size distribution of the solids in the bed, the surface properties of the fuel which composes it, and the mechanical forces to which it is subjected. Thus far there appears to be little more than theoretical knowledge of this subject,[106] although some experimental work on flow properties of such beds is now becoming available.[84, 85] Only in the work of Bennett and Brown,[86] however, does the suggestion appear that the void volume of the bed controls the path of gas flow and is, in turn, partly controlled by it, and that, furthermore, large fractional void volumes may be confined to a particular region within the bed by making use of the mechanical properties of flowing beds of broken solids to control segregation.

It is evident from the discussion above that estimates of thermal properties of the materials forming the fuel bed and passing through it are required for the analysis. Conductivity and specific heat of the fuel are considered elsewhere;[107] the heat-transfer coefficient between solids and gases in the bed has been mentioned above;[88] estimates of the heat capacity[108] and viscosity[109] of the bed gases are also available.

105 Bennett, J. G., J. Soc. Glass Tech., 23, 154–70 (1939).

106 Fuller, W. B., and Thompson, S. E., Trans. Am. Soc. Civil Engrs., 59, 67–172 (1907). Furnas, C. C., U. S. Bur. Mines, Rept. Investigations, 2894 (1928), 10 pp. Westman, A. E. R., and Hugill, H. R., J. Am. Ceram. Soc., 13, 767–79 (1930). Manegold, E., Hofmann, K., and Solf, K., Kolloid-Z., 56, 142–59 (1931). Meldau, R., Z. Ver. deut. Ing., 76, 1189–95 (1932). Meldau, R., and Stach, E., J. Inst. Fuel, 7, 336–54 (1934). Stückel, W., and Radt, W. P., Brennstoff-Chem., 15, 121–6 (1934). Koeppel, C., Glückauf, 73, 369–78 (1937). Anderegg, F. O., Bull. Am. Ceram. Soc., 16, 11–3 (1937). White, H. E., and Walton, S. F., J. Am. Ceram. Soc., 20, 155–66 (1937).

107 Chapter 7.

108 Chipman, J., and Fontana, M. G., J. Am. Chem. Soc., 57, 48–51 (1935). Brückner, H., Gas- u. Wasserfach, 78, 637–9 (1935). Brückner, H., and Bender, W., ibid., 79, 701–5 (1936). Murphy, G. M., J. Chem. Phys., 5, 637–41 (1937). Fenning, R. W., and Whiffen, A. C., Phil. Trans. Roy. Soc. (London), A238, 149–212 (1939). Swelgert, R. L., and Beardsley, M. W., Georgia State Eng. Expt. Sta., Bull. 2 (1938), 11 pp.; Mech. Eng., 61, 389–90 (1939).

109 Bremond, P., Compt. rend., 196, 1472–4 (1933).

FURNACE VOLUME REACTIONS

In all grate-fired furnaces, the last portion of the combustion process takes place in the furnace above the fuel bed. There has been relatively little study of this process, although the development of high boiler settings, and the increase in stoker ratings attained after their introduction, in the 1920's, attest to the importance of this portion of the combustion process. Combustion in the furnace is responsible for two functions: (1) to burn out the carbon remaining in particles of fly coke ejected from the bed by the high velocity of gas flow; and (2) to burn the combustible gas flowing out of the bed, resulting either from carbonization processes occurring in the bed or from incomplete combustion of carbon monoxide or hydrogen.

From the point of view of securing rapid completion of these reactions, the furnace is an ineffective reaction space because of the relatively low velocity of flow through it and the relatively large cross section of the gas stream with respect to its length, which leads to stratification or the existence of great disparities in the composition of the gases at points in the same cross section. Close to the furnace exit there may be sections of the stream containing relatively large concentrations of combustible gas alongside of filaments containing large concentrations of oxygen, so that neither filament has completed its work. Still, because of the slow velocity of mixing associated with the low gas velocity, compared with the large cross sections of these filaments, the stream may leave the furnace and enter a relatively cool space, where reaction cannot proceed at any considerable speed without these filaments combining to produce complete combustion.

The burning-out of particles of fly coke probably is governed by the same laws as pulverized-coal-firing.[110] The factors affecting the rate at which the gas burns out in the furnace were partially investigated by Kreisinger and his coworkers.[111] Though a complete analysis of the process is not available, the hydrodynamics of the system have been studied in model experiments in Germany [112] and in many cases the results have been checked in traveling-grate-fired furnaces in practice [26] by the application of high-pressure overfire air jets as indicated by the experiments. The engineering application is now being extended in this country [34] but this is carried out largely on an empirical basis without benefit of theoretical or model investigations. It appears from the German work that, in this system, the gross mixing rates of the furnace atmosphere are the most important factors in determining the rate of burning-out of furnace gases. There has been no indication that any other data [113] than the rate at which the mixing is brought about are significant for an estimate of the effectiveness in producing complete combustion of a given method of producing mixing. There is, however, no satisfactory measure of such an effectiveness of mixing, so the last statement must be considered as qualitative, only.

[110] Cf. Chapter 34.
[111] Clement, J. K., Frazer, J. C. W., and Augustine, C. E., *U. S. Bur. Mines, Tech. Paper* **63** (1914), 46 pp. Kreisinger, H., Augustine, C. E., and Ovitz, F. K., *U. S. Bur. Mines, Bull.* **135** (1917), 144 pp.
[112] Rummel, K., and Schwiedessen, H., *Arch. Eisenhüttenw.*, **6**, 543–9 (1933). Marcard, W., *Arch. Wärmewirt.*, **14**, 262–4 (1933) ; *Mech. Eng.*, **56**, 235–7 (1934). Hoerner, S., *Z. Ver. deut. Ing.*, **80**, 949–57 (1936). Rummel, K., *Arch. Eisenhüttenw.*, **10**, 505–10, 541–8, **11**, 67–80, 114–23 (1937) ; *Fuel*, **17**, 287–8 (1938). Marcard, W., *Wärme*, **60**, 257–66 (1937). Schiegler, L., *Z. Ver. deut. Ing.*, **82**, 849–55 (1938) ; *Fuel*, **18**, 221 (1939). Koessler, P., *Arch. Wärmewirt.*, **19**, 153–6 (1938).
[113] Lewis, B., and von Elbe, G., *Combustion, Flames and Explosions of Gases*, Cambridge Univ. Press, London, 1938, 415 pp.

In a fuel bed, the temperatures are less completely determined by the *external* heat transfer than they are in a powdered-fuel furnace, but the temperature in the open furnace is largely determined by this factor. The relative independence of the bed temperatures is caused by the fact that conductivity of the bed is responsible for only a fraction of the heat flow due to convection, except where the temperature gradients are very large. Thus, at the end of the fuel-bed gas path where the gas enters the furnace, where the reactions are nearly complete, conduction along the path of the gas flow is relatively small, and the temperature at any point is almost completely determined by the heat content of the gas flowing to that point, and so by the extent to which the reactions have proceeded at earlier points in the path. At this end of the gas path, the solids of the bed do lose heat to the distant furnace walls or cold surface, and this loss is made up partly by conduction from the immediately adjacent portions of the bed and partly by the gas convection. Because of the small ratio of the heat flow by conduction to that by convection, however, this effect does not extend far from the furnace end of the bed. This characteristic is shown by the bed temperatures observed by Nicholls.[95]

In the open furnace, on the other hand, the change in temperature is entirely determined by a balance between the heat released at a point and the interchange of heat with the surroundings, largely by radiation. The temperature at any point in the furnace is of great importance in determining the incidence of troubles at that point due to slagging, and to some extent due to clinkering, though the latter are more dependent on fuel-bed temperatures. It also helps to determine the tem-

perature and composition of the gases entering the convection surface of the boiler, heater, etc. The problem of slagging is great enough to command an entire report in this monograph, so no attempt will be made to treat it here.[114] Heat transfer in the furnace takes place mainly by way of radiation, though there undoubtedly is a small contribution due to convection.[115] It is to be noted that, in order to estimate the heat lost from the furnace side of the fuel bed, an accurate map of the surface temperatures of the bed would be necessary. It probably may be assumed that the fuel-bed radiation would be essentially "gray," that is, proportional to that produced by a "black body" at the same temperature, and having emission coefficient fairly close to unity. Previous estimates of fuel-bed radiation to cold surface have probably been greatly in error, as it has been customary to assume a uniform radiating temperature for the entire surface. The studies previously referred [26, 29, 99, 100] to have provided the information necessary to make more realistic estimates of surface temperature so that better estimates of heat transferred from the bed to cold surface are now possible.

[114] Cf. Chapter 15.
[115] Schmidt, E., *Z. Ver. deut. Ing.*, **76**, 1025–32 (1932). Geck, W., *Gas- u. Wasserfach*, **76**, 817-23, 833 40 (1933). Mullikin, H. F., *Trans. Am. Soc. Mech. Engrs.*, **57**, 517–29 (1935). Wohlenberg, W. J., and Mullikin, H. F., *ibid.*, **57**, 531–40 (1935). Wohlenberg, W. J., Mullikin, H. F., Armacost, W. H., and Gordon, C. W., *ibid.*, **57**, 541–54 (1935). Heiligenstaedt, W., *Gas- u. Wasserfach*, **79**, 754–60, 783–8 (1936). Eberhardt, J. E., and Hottel, H. C., *Trans. Am. Soc. Mech. Engrs.*, **58**, 185–93 (1936). Hottel, H. C., Meyer, F. W., and Stewart, I. McC., *Ind. Eng. Chem.*, **28**, 708–10 (1936). Michel, F., *Feuerungstech.*, **24**, 77–8 (1936). Eckert, E., *Arch. Wärmewirt.*, **18**, 107+8 (1937). Orrok, G. A., and Artsay, N. C., *Combustion*, **9**, No. 10, 37–42 (1938). Koch, B., *Feuerungstech.*, **27**, 137–41 (1939). Jakob, M., and Hawkins, G. A., *J. Appl. Phys.*, **13**, 246–54 (1942).

CHEMISTRY OF COMBUSTION

STOICHIOMETRY

The end products of combustion reactions and the heat quantities involved are relatively simple, being confined to carbon dioxide and water vapor in a complete reaction, but nevertheless there continue to appear, in the engineering periodicals devoted to combustion, articles describing "new" methods of calculating these quantities. There is no point to giving an exhaustive list of these here, but some outstanding examples will be referred to.

The fundamental calculations are easily available.[3, 63] A good résumé of simplified methods of calculation was presented in a special section of *Power* magazine in 1940.[116] Rosin[117] developed the so-called *IT* diagram for convenience in combustion calculations, but the temperatures calculated by its use probably are of no significance in the combustion process. They certainly do not represent temperatures attained anywhere in a real furnace. In the way of combustion calculations there has even been given a design of slide rule for speedy computation.[118]

Dolch, Fehling, and Thring[119] have described methods of calculating gas composition and heat release in incomplete combustion.

KINETICS OF COMBUSTION REACTIONS

The chemistry of the heterogeneous reactions between carbonaceous surfaces and oxidizing gases has been thoroughly reviewed.[80, 120] The subject had been investigated from the early days of chemistry, but, until Rhead and Wheeler's hypothesis of the C_xO_y complex,[121] the investigations revolved about polemics concerning which of the two oxides was primary and whether traces of water were essential for the reaction.[122] The interest in the subject did, however, yield some fairly good measurements of reaction rates, especially of the reduction of carbon dioxide.[123]

Rhead and Wheeler's[121] and, subsequently, Langmuir's high-vacuum work[124] showed that highly purified carbon surfaces were capable of holding oxygen even at combustion temperatures. It had long been appreciated that such surfaces could retain oxygen at relatively low temperatures and that, on removal, a large proportion of the oxygen came off only as oxides of carbon.[125] Rhead and Wheeler showed, by determining the rate of reduction of carbon dioxide in a well-thermostated system and subsequently measuring the concentration of carbon oxides produced by the action of oxygen, that both carbon monoxide and carbon dioxide must be considered primary

[116] Anon., *Power*, **84**, 773–804 (1940).

[117] Rosin, P., and Fehling, H. R., *Das IT-Diagramm der Verbrennung*, Ver. deut. Ing. Verlag, Berlin, 1929, 32 pp. Kay, H., *J. Inst. Fuel*, **9**, 312–22 (1936).

[118] Boie, W., *Feuerungstech.*, **24**, 189–91 (1936). Lenhart, E., *ibid.*, **25**, 265–73 (1937).

[119] Dolch, P., *Feuerungstech.*, **27**, 109–12 (1939). Fehling, H. R., *J. Inst. Fuel*, **14**, 39–46 (1940). Thring, M. W., *Fuel*, **20**, 64–9 (1941).

[120] Strickland-Constable, R. F., *Fuel*, **19**, 89–93 (1940). Bangham, D. H., and Bennett, J. G., *ibid.*, **19**, 95–101 (1940).

[121] Rhead, T. F. E., and Wheeler, R. V., *J. Chem. Soc.*, **101**, 831–45, 846–56 (1912); **103**, 461–89, 1210–4 (1913).

[122] Baker, H. B., *J. Chem. Soc.*, **47**, 349–52 (1885). Lang, J., *Z. physik. Chem.*, **2**, 161–83 (1888). Dixon, H. B., *J. Chem. Soc.*, **75**, 630–9 (1899). Armstrong, H. E., *J. Soc. Chem. Ind.*, **24**, 473–82 (1905).

[123] Naumann, A., and Pistor, C., *Ber.*, **18**, 1647–57 (1885). Boudouard, O., *Bull. soc. chim.*, (3), **21**, 465–7, 713–5 (1899), **25**, 833–40 (1901); *J. Soc. Chem. Ind.*, **20**, 1196 (1901). Farup, W., *Z. anorg. Chem.*, **50**, 276–96 (1906). Clement, J. K., Adams, L. H., and Haskins, C. N., *Univ. Ill. Expt. Sta., Bull.* **30** (1909), 46 pp.

[124] Langmuir, I., *J. Am. Chem. Soc.*, **37**, 1139–67 (1915).

[125] Baker, C. J., *J. Chem. Soc.*, **51**, 249–58 (1887). Porter, H. C., and Ralston, O. C., *U. S. Bur. Mines, Tech. Paper* **65** (1914), 80 pp.

products. Langmuir showed that high-vacuum technique could entirely eliminate the incidence of secondary reactions. This tool was used by Eucken [126] and his students in investigations of the mechanism of combustion of graphitic carbon by oxygen, carbon dioxide, water vapor, and nitric oxide. Meyer [127] found, in experiments carried out at pressures of the order of 10^{-3} millimeter of mercury in flowing gases, that oxygen reacted with carbon filaments to give equimolecular quantities of carbon monoxide and carbon dioxide in a first-order reaction up to temperatures of the order of 1,500° C, while, at temperatures above that, 2 moles of carbon monoxide were produced for each mole of carbon dioxide in a zero-order reaction. These results were substantiated in further work.[128, 129] It was also shown that the electric resistance of carbon filaments exposed to oxygen at combustion temperatures increased, suggesting the adsorption of oxygen; and that carbon dioxide and water vapor reacted with carbon filaments in a zero-order reaction, having a heat of activation of 90 kilocalories.

Sihvonen found qualitatively similar results, although they differed in detail, at least partly because the filaments used by Sihvonen were less uniform than those used by Meyer. Sihvonen was an unusually prolific writer for this field, and only a few of his articles are listed herewith; [130] the last

citation gives a complete list of his publications.

Mechanisms for these reactions were proposed by the authors which involved the holding of oxygen to graphitic surfaces by primary or secondary valences. Meyer's and Eucken's analysis tended toward the latter, suggesting an adsorption of oxygen molecules linked across two carbon atoms in the graphite hexagon, which were subsequently released by the impingement of another oxygen molecule from the gas phase. Sihvonen's mechanisms suggested the formation of keto- and ketene groups through primary valence reactions, these groups subsequently being evaporated. It seems likely that a clearer picture of the nature of the bound oxygen and perhaps of the kinetics of its release may result from a correlation of the extensive studies of adsorptive carbons discussed below. Before leaving the work of this school, however, it should be noted that the reaction rates found by Meyer, even though of the first order, could not account for the rates of burning measured by those who worked at atmospheric pressure by a factor greater than 10.[80, 129] A possible explanation of this fact is that the carbons used in the atmospheric pressure work were so porous that a very extensive internal surface was available for reaction.[131]

Considerable work has been done on the rates of the oxidizing reactions at normal pressures, mainly in connection with estimates of the reactivity of coke.[132] Results of special significance with respect to the chemical mechanisms involved have been obtained from measurements with air or

[126] Eucken, A., *Z. angew. Chem.*, **43**, 986–93 (1930).

[127] Meyer, L., *Z. physik. Chem.*, **B17**, 385–404 (1932).

[128] Meyer, L., *Z. Elektrochem.*, **40**, 640–1 (1934). Martin, H., and Meyer, L., *ibid.*, **41**, 136–46 (1935). Boersch, H., and Meyer, L., *Z. physik. Chem.*, **B29**, 59–64 (1935).

[129] Meyer, L., *Trans. Faraday Soc.*, **34**, 1056–61 (1938).

[130] Sihvonen, V., *Z. Elektrochem.*, **36**, 806–7 (1930), **40**, 456–60 (1934); *Brennstoff-Chem.*,

17, 281–5 (1936); *Trans. Faraday Soc.*, **34**, 1062–74 (1938).

[131] Cf. ref. 76 (1939) and ref. 90 (1942). Thiele, E. W., *Ind. Eng. Chem.*, **31**, 916–20 (1939).

[132] See Chapter 24.

oxygen,[133] with carbon dioxide,[134] and with steam, nitric oxide, etc.[135]

A large amount of work on the kinetics of these reactions has been done by the Russians.[93, 136] Frank-Kaminetskii's observations on the reduction of carbon dioxide appear to be in agreement with previous work.[80, 120] Unless, however, the experimental observations are given in much greater detail in the Russian articles than in the available English translations, it appears that Chukhanov's interpretations cannot be given great weight. The division of the combustion mechanism into two steps, the so-called oxidation and combustion reactions, was based on experiments in which a suspension of charcoal in air or oxygen was passed through a heated furnace. In the neighborhood of 700° the

evolution of carbon monoxide was said to increase abruptly. In this type of experiment, secondary reactions are not excluded; furthermore, the temperature was not uniform throughout the furnace, so that the results should be examined in the light of an analysis of reaction rates in nonisothermal fields.[137] Under the circumstances, the observations do not seem to demand a particular solution for their adequate statement, so that, even though Chukhanov's analysis did represent the data, that analysis could hardly be considered unique.

There has been in the past no indication of the existence of a marked velocity coefficient of the formation of carbon monoxide,[93] although velocities have been attained in fuel beds of the same order as the lower ones reached in Chukhanov's experiments. The appearance of somewhat increased carbon monoxide at high velocities was to be expected on the grounds of the conventional picture of the combustion of carbonaceous phases in which both carbon monoxide and carbon dioxide are formed at the reacting surface, the carbon monoxide being oxidized further in its diffusion out into the main gas stream. Such a picture was based on Tu, Davis, and Hottel's[75] observation of a blue halo about their burning sphere and on the observation of a steady blue flame approximately midway in a fixed diffusion path apparatus orally reported by S. P. Burke. On the other hand, Parker and Hottel[79] found no evidence of any carbon monoxide in their microsampling experiments. Although their analysis of the transport phenomenon may be criticized through its failure to take account of oxygen and carbon dioxide flow by convection, which renders suspect the significance of the concentration gradients

[133] Oshima, Y., and Fukuda, Y., *Proc. 3rd Intern. Conf. Bituminous Coal*, **2**, 448–84 (1931). Godbert, A. L., *Safety Mines Research Board* (*London*), *Paper* **68**, (1931), 9 pp. Blayden, H. E., and Riley, H. L., *Gas World*, **99**, Coking Sect., 116–21 (1933). Lambert, J. D., *Trans. Faraday Soc.*, **32**, 452–62 (1936).

[134] Oshima, Y., and Fukuda, Y., *J. Soc. Chem. Ind.* (*Japan*), **32**, Suppl. binding, 208–10, 226–7, 251–2 (1929); *Fuel*, **9**, 5, 200 (1930). Broom, W. E. J., and Travers, M. W., *Proc. Roy. Soc.* (*London*), **A135**, 512–37 (1932). Bolland, C. B., and Cobb, J. W., *J. Soc. Chem. Ind.*, **52**, 153–9T (1933). Blakeley, T. H., and Cobb, J. W., *Inst. Gas Engrs., Commun.* **104** (1934), 49 pp. *Gas J.*, **208**, 351–3, 526–7, 748–9 (1934). Mayers, M. A., ref. 76.

[135] Key, A., and Cobb, J. W., *J. Soc. Chem. Ind.*, **49**, 439–44T (1930). Meyer, L., *Naturwissenschaften*, **20**, 791 (1932); *Brennstoff-Chem.*, **14**, 33 (1933). Strickland-Constable, R. F., *Trans. Faraday Soc.*, **34**, 1374–80 (1938).

[136] Grodzovskii, M. K., and Chukhanov, Z. F., *Compt. rend. acad. sci. U.R.S.S.*, **3**, 356–9 (1934). Grodzovskii, M. K., and Chukhanov, Z. F., *Khim. Tverdogo Topliva*, **7**, 902–19, 986–98 (1936); *J. Appl. Chem.* (*U.S.S.R.*), **9**, 73–81 (1936); *Fuel*, **15**, 321–8 (1936). Chukhanov, Z. F., *J. Tech. Phys.* (*U.S.S.R.*), **8**, 147–61; 621–32 (1938); *Fuel*, **18**, 292–302 (1939), **19**, 17–20, 49–50, 64–7 (1940). Frank-Kaminetskii, D. A., *Compt. rend. acad. sci. U.R.S.S.*, **23**, 663–5 (1939); *Chem. Abs.*, **34**, 4648 (1940).

[137] Sherman, J., *Ind. Eng. Chem.*, **28**, 1026–31 (1936).

they observed, it seems that they should still have found carbon monoxide close to the particle surface if any was formed. The fact that the first-order reaction rates, referred to the surface oxygen concentration, gave a unique Arrhenius correlation on the assumption of zero monoxide formation, and failed to do so if the monoxide was assumed to be present, supports their experimental observations. For the time being, it seems advisable to accept Chukhanov's observations, pending their confirmation by independent observations; acceptance of his interpretation may, however, be suspended until critical experiments can be made to distinguish between the mechanism he proposed and such physical factors as those suggested by Thring.[94]

Investigations into the nature of active carbon surfaces [138] have produced a quantity of information which, although still uncorrelated with kinetic studies, may be expected eventually to throw some light on the nature of the carbon-oxygen surface complex. Oxygen admitted to a clean carbon surface is very strongly held, the initial increments having heats of adsorption of up to 90 kilocalories per mole. This adsorption goes on at a slow rate apparently because of relatively slow diffusion to more remote portions of the carbon surface. It can be removed only by evacuation at elevated temperatures when the oxygen is recovered in the form of oxides of carbon. When, however, a surface which is thoroughly saturated with oxygen is pumped off without raising the temperature, fresh oxygen admitted is adsorbed

physically only and may be recovered by pumping.

Other work has shown that oxidized carbon surfaces may have either acid or basic properties.[139] Related results were obtained by Lambert and Strickland-Constable,[140] who classified the surface oxides on carbon as of labile and stable types. The stable oxides retard the oxidation, while the normal reaction proceeds through the labile type. This point of view is similar to the position taken by Polanyi,[141] who pointed out that catalysis is favored by weak rather than by strong adsorption, since strongly adsorbing active surfaces removed themselves from the kinetic field by being stably covered with reagent. Strickland-Constable, in supporting his thesis that the surface oxides are of at least two different kinds, stressed the reasonable supposition that, if the formation of the same oxides as produce the extraordinary heats of reaction observed by Garner and McKie,[138] and are so strongly held that they are removed only by evacuation at temperatures above 1,000°, were responsible for the oxidation of graphite, the reaction would be of zero order, and would take place relatively slowly since only a small portion of the exposed surface would be, at any moment, available for reaction. But, in fact, the oxidation reactions are

[138] Lowry, H. H., and Hulett, G. A., *J. Am. Chem. Soc.,* **42**, 1408–19 (1920). Garner, W. E., and McKie, D., *J. Chem. Soc.,* **1927**, 2451–7. Keyes, F. G., and Marshall, M. J., *J. Am. Chem. Soc.,* **49**, 156–73 (1927). Lamb, A. B., and Ohl, E. N., *ibid.,* **60**, 1287–90 (1938), **61**, 528 (1939). Muller, S., and Cobb, J. W., *J. Chem. Soc.,* **1940**, 177–83. Marshall, M. J., and Findlay, R. A., *Can. J. Research,* **18B**, 85–43 (1940).

[139] Shilov, N., and Chmutov, K., *Z. physik. Chem.,* A148, 233–6 (1930). Shilov, N., Shatunovska, H., and Chmutov, K., *ibid.,* A149, 211–22 (1930). King, A., *J. Chem. Soc.,* **1933**, 842–6, **1934**, 22–6. King, A., and Lawson, C. G., *Trans. Faraday Soc.,* **30**, 1094–103 (1934). King, A., *J. Chem. Soc.,* **1934**, 1975–80, **1935**, 889–94, **1936**, 1688–92. Hofmann, U., and Rüdorff, W., *Trans. Faraday Soc.,* **34**, 1017–21 (1938). Riley, H. L., *ibid.,* **34**, 1011–6 (1938). Larsen, E. C., and Walton, J. W., *J. Phys. Chem.,* **44**, 70–85 (1940).
[140] Lambert, J. D., *Trans. Faraday Soc.,* **34**, 1080–2 (1938). Strickland-Constable, R. F., *ibid.,* **34**, 1074–80 (1938).
[141] Polanyi, M., *J. Soc. Chem. Ind.,* **54**, 123–4T (1935).

found to be of the first order with respect to the oxidizing gas concentration;[121, 127, 128, 130] even the oxidations by carbon dioxide and steam, which were found to be of zero order in vacuum apparatus,[128, 130] are of the first order at atmospheric pressure in experiments in which the gas is always at the temperature of the reacting surface.[76, 94] It may be hoped that more complete analyses of the kinetics of sorption[142] may help to clarify some of these anomalies.

In summary, then, it may be considered that the mechanism of oxidation of graphite by gases is still a largely unsolved problem. The lines of attack are laid out, and the general nature of many of the ultimate characteristics of the reaction scheme are already known, but the job of digging out the details and substantiating them remains to be done. There appear to be two methods that should be pursued in parallel: one is the investigation at normal pressures, by means of Mayers'[76, 120, 143] scheme of increasing gas velocities until the observed rate of reaction reaches and remains at a maximum value; the other involves vacuum methods and can probably be reduced to still better control by the use of a "molecular beam" type of apparatus,[144] which permits control of gas temperature as the Sihvonen or Meyer apparatus does not[128, 129, 130] and which may permit the attainment of higher effective beam concentrations than in that appa-

ratus without serious incidence of secondary reactions.

All the material discussed above was concerned with the reaction of gaseous oxidizing agents with graphite, or sensibly graphitic forms of carbon. The general thesis is probably acceptable that there is no definite dividing line between graphite on the one hand and the rather highly condensed carbonaceous materials represented by cokes and chars and other highly condensed polycyclics on the other.[145] This does not, however, permit an extension from a sketchily known mechanism on graphite, through an unexplored connection between graphite and coal, to an estimate of the nature of the reaction between coal and oxidizing gases. It is known that coal is capable of absorbing oxygen at low temperatures and retaining it very strongly,[146] and that oxygen so absorbed is recovered largely in the form of oxides of carbon and water vapor, on heating, in analogy with the behavior of graphitic materials. Such absorption proceeds at a decreasing rate as the coal becomes more thoroughly covered, just as the low-temperature reactions proceed on graphitic materials; on the other hand, the oxidation causes gross changes in the nature of the coal, altering its characteristics on carbonization in the direction of decreasing rank.[147]

It is probably true that all coals have been converted to coke before the rates of their rapid burning become of interest, and

142 Wilkins, F. J., *Proc. Roy. Soc. (London)*, A104, 496–509 (1938). Kimball, G. E., *J. Chem. Phys.*, 6, 447–53 (1938). Laidler, K. J., Glasstone, S., and Eyring, H., *ibid.*, 8, 659–67, 667–76 (1940).

143 Khaikina, S. E., *J. Tech. Phys. (U.S.S.R.)*, 8, 53–64 (1938). Vulis, L. A., and Vitman, L. A., *ibid.*, 11, 509–18 (1941); *Chem. Abs.*, 35, 6502 (1941).

144 Fraser, R. G. J., *Molecular Rays*, Cambridge Univ. Press, London, 1931, 204 pp.

145 Hofmann, U., and Sinkel, F., *Z. anorg. allgem. Chem.*, 245, 85–102 (1940).

146 Porter, H. C., and Ralston, O. C., ref. 125. Newall, H. E., *Fuel*, 14, 160–7 (1935). Krym, V. S., *Khim. Tverdogo Topliva*, 8, 461–72 (1937); *Chem. Abs.*, 32, 1428 (1938). Krym, V. S., and Semenikhin, S. I., *Khim. Tverdogo Topliva*, 8, 782–5 (1937); *Chem. Abs.*, 32, 2319 (1938). Holmes, C. R., Brewer, R. E., and Davis, J. D., *Ind. Eng. Chem.*, 32, 792–7, 980–4 (1940).

147 See Chapters 18 and 23.

in this form it seems likely that their reactions are nearly enough like those of graphite so that studies of this material may be extended to them. On the other hand, heat release by the coal itself may be important in the initial stages of heating leading to ignition in many types of apparatus; it almost certainly is in pulverized-coal firing. For this reason, reaction rates of coals at relatively low temperatures, but still high enough so that the reaction proceeds continuously, are of considerable interest. Apparatus for this measurement is available,[148] by means of which the rates of the oxidation of many coals and cokes have been determined. The apparent heat of activation of the reaction is found to change regularly with the rank of the coal, being quite small, of the order of 12,000 calories, for low-rank bituminous coals and lignites, increasing to values of about 18 kilocalories for high-rank bituminous coals and anthracite and then to nearly 30 kilocalories for high-temperature coke. This determination assumes that the reaction is of the first order as it is ordinarily carried out, by making observations in systems containing different concentrations of oxygen, usually 100 percent, and that of air, 21 percent. The assumption, however, has been checked by making multiple observations in which the rate of heating is varied and has been found to be true for coals and for cokes not treated with soda. There is no question of transport of the oxidizing gas entering the picture at the low reaction rates involved in this determination, so the conclusion as to the order must apply directly to the primary process. When, however, the reaction rates of cokes treated with alkalies or alkali carbonates were determined, it was found that, not only was the reaction rate materially increased, in agreement with other work, but the reaction was found to fall off from unit order, with increasing oxygen concentration, toward a reaction of zero order for oxygen pressures slightly greater than atmospheric.[149]

CONCLUSION

The combustion of solid fuel is a chemical process for making available the heat of combustion of a variety of solid carbonaceous materials which are extensively used as a source of power. Commercially, however, the rates of burning attained are conditioned not by the rates of the chemical reactions but by the arrangement of the various parts of the combustion apparatus. This has been developed empirically by the exercise of the inventor's art. Further advances may be expected, however, by directed study of the factors limiting the process in existing types of equipment. Such studies must be concerned primarily with the physical, rather than the chemical, limitations imposed by the system.

Problems which call for practical solutions include: (1) control of the rates of carbonization and ignition in fuel beds, including the factors which result in smoke production and in coke-tree formation; (2) control of temperature at various zones in fuel beds—the crux of the clinker problem —the achievement of which might result in new standards of gas production practice; and (3) control of furnace reactions above the fuel bed.

The solution of these problems requires better measurements of the reaction rates in beds of broken solids, and their behavior near the limits of bed stability;

148 Sebastian, J. J. S., and Mayers, M. A., *Ind. Eng. Chem.*, **29**, 1118–24 (1937). See Chapter 24.

149 Sebastian, J. J. S., *Symposium on Combustion of Solid Fuel*, Boston Meeting, American Chemical Society, September 12, 1939, pp. 37–40.

accurate determinations of heat transfer in, and conductivity of, such beds; adequate analytical methods for the interpretation of experimental results of tests on fuel beds; and the development of criteria of similarity so that model tests of determinable significance can be made both on fuel beds, especially for the flow of particulate materials, and on combustion spaces.

On the other hand, continued engineering development is required to elaborate new devices capable of satisfying the more exacting requirements that such advances will impose; able to produce the forces required to control the flow of broken solids and to avoid, or control, segregation; and to facilitate utilization of such new principles of gas or heat production as may appear from continued investigations. Furthermore, engineering analysis is needed for the full utilization of existing equipment and fuel resources to the end that the overall best results may be obtained for minimum expenditures.

THE COMBUSTION OF PULVERIZED COAL

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The use of pulverized coal has developed largely as an industrial art. The literature is filled with descriptions of equipment, reports of operating experiences, and test data. Knabner's comprehensive bibliography of the literature up to 1930[1] contains relatively few references to theoretical or experimental papers on the principles of combustion.

The early history of the use of pulverized fuel is vaguely defined. The failure to comprehend the burning of solid fuel while suspended in air, as a distinctive method of firing, as well as the lack of knowledge of the technical requirements, contributed to its slow development.[2]

The first important industrial development[3] followed the experiments of Hurry and Seaman of the Atlas Portland Cement Company in 1894. The universal adoption of pulverized coal throughout the cement industry,[4] except where local market conditions favor oil or gas, is evidence of their success, but the reluctance of cement manufacturers to disclose their methods contributed to the continued slow development. It was not until 1900 that it became generally known that they were using pulverized coal.

A typical cement kiln is a refractory-lined tube up to 10 feet in diameter and 100 to 400 feet in length. The slope and rotation of the tube are such as to keep the lining covered by the cement as it flows through the kiln. Temperatures near the burner are high,[5] above 2,400° F, aiding the ignition process and bringing about re-ignition in the event of momentary stoppage of coal supply. A comparatively low rate of heat release, about 7,000 Btu per hour per cubic foot of total kiln volume, indicates that ample time is available for complete combustion. The coal ash presents no difficulty; it is largely absorbed in the cement, and, being similar in nature, simply adds to the production.

[1] Knabner, O., *Auf das Schrifttum Kohlenstaub, eine Zusammenstellung der einschlägigen Veröffentlichungen*, Verlag Ver. deut. Ing., Berlin, 1930, 116 pp.

[2] Crampton, T. R., *J. Iron Steel Inst.*, **7**, 91–101 (1873). Anon., *Engineering*, **61**, 80–1 (1896). Low, F. R., *Trans. Am. Soc. Mech. Engrs.*, **36**, 123–36 (1914). Brooks, H. W., *Mech. Eng.*, **47**, 89–93 (1925). Renkin, W. O., *Trans. Fuel Conf., World Power Conf., London*, **3**, 407–37 (1928). Ehmig, J., *Wärme*, **62**, 377–80 (1939). See also Harvey, L. C., *Pulverised Fuel, Colloidal Fuel, Fuel Economy, and Smokeless Combustion*, Macmillan Co., New York, 1924, 466 pp.

[3] Carpenter, R. C., *Trans. Am. Soc. Mech. Engrs.*, **36**, 85–107 (1914). Herington, C. F., *Combustion*, **7**, 845–50, 862 (1922), **8**, 42–8 (1923).

[4] Hardgrove, R. M., *Am. Inst. Mining Met. Engrs., Tech. Pub.* **1390** (1941), 9 pp.; *Mining Technology*, **5**, No. 6, T.P. 1390 (1941), 9 pp.

[5] Bailey, E. G., *Proc. Ninth Fuel Engrs. Meeting, Appalachian Coals, Inc.*, **2**, 182–209 (1935). Reaser, W. E., *Trans. Am. Soc. Mech. Engrs.*, **64**, 265–71 (1942).

Although a momentary loss of ignition caused no difficulty, a complete loss often caused cooling stresses, loosening patches of refractory in a kiln which otherwise might have operated for a considerably longer time. This condition caused the cement industry to place emphasis on reliability of operation. Since early pulverizers were not reliable in continuous operation, the bin and feeder system was almost universally adopted. In this system the pulverizers are operated a few hours a day and the pulverized coal is stored until needed. In order to prevent packing in the pulverized-coal bins it is necessary to dry the coal carefully. Wet coal also reduces pulverizer capacities and increases the difficulty of distributing the coal in the air at the burners.

Figure 1 shows typical cement-kiln installations and contrasts the simplicity of the more modern direct-fired system with the complexity of the bin and feeder system. The direct system has been made possible by improvements in pulverizer design. The costly and cumbersome coal drier has been replaced by sweeping hot air through the pulverizer. This hot air evaporates the moisture from the coal and also carries the fine coal through the classifier and into the furnace.

About 1903 the American Iron and Steel Manufacturing Company,[6] noting the successful use of pulverized coal in the cement industry, started experimental work on its application to their metallurgical furnaces.

6 Lord, J., *Proc. Engrs Soc. West. Penna.,* 29, 361–71 (1913).
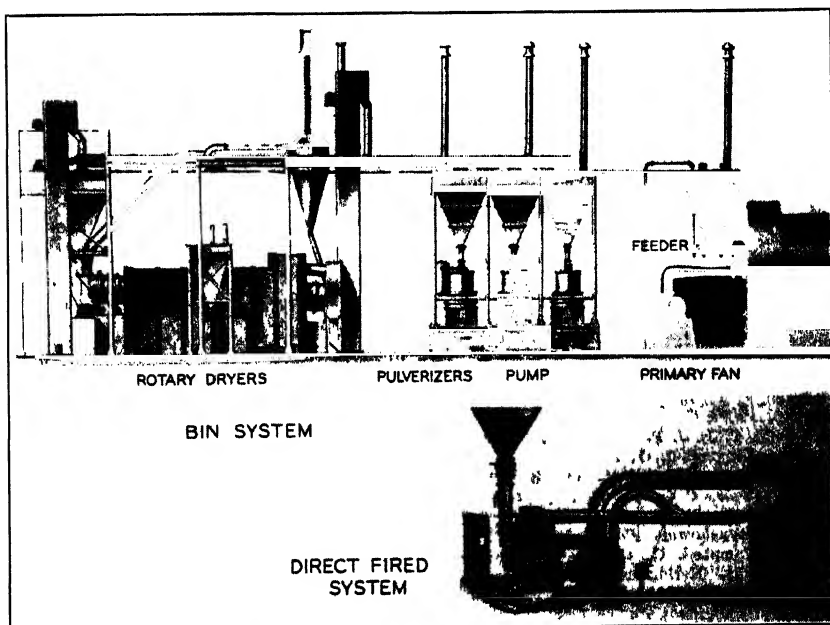
FIG. 1. Typical cement kiln installations. (Courtesy of the Babcock & Wilcox Company.)

Their early work was not very encouraging. They tested almost every available type of burning equipment without much success. They finally began to realize that success depended on the proper choice of operating variables rather than any special design of burner. In presenting the results of their work, Lord emphasized the necessity of careful drying, sufficiently fine pulverization, and good feed control from the storage bin to the burner, but gave practically no information on burner design except that burners had been adapted to rates of coal feed ranging from 40 to 900 pounds of coal per hour.

The metallurgical industry has contributed very little technical advancement to the use of pulverized coal. Its principal service has been to rediscover the methods employed by the cement industry and to disseminate information on methods and applications suited to the use of pulverized coal.[7] The periods of active development have coincided with those during which there was a scarcity of "more desirable" fuels. The failure to achieve any real advancement appears to have been due to an attempt to adapt pulverized coal to existing types of furnaces rather than adapting the furnaces to the use of pulverized coal.

The copper reverberatory furnace is an outstanding example of the successful application of pulverized coal to metallurgical furnaces.[8] Furnaces of this type are generally fired from one end and have sufficient length, frequently over 100 feet, so that there is ample time for the coal dust to burn. In some furnaces the burners discharge directly over the melt; in others a chamber is provided so that ignition and partial combustion are complete before the flame reaches the main furnace. Contamination by ash can be minimized by fine pulverization and high gas velocities.

Certain types of small metallurgical furnaces, requiring controlled high temperature rather than high thermal efficiency, are suited to pulverized-coal firing.[9] These furnaces are most often fired with oil or gas, but local shortages of these fuels have made it advisable to consider the use of pulverized coal.

By 1920, the use of pulverized coal was well established in the cement industry and had found many applications in metallurgical furnaces. A considerable variety of equipment was available for the preparation and handling of pulverized coal.[10] However, almost without exception successful and economical application involved either a large combustion space ideally suited to the pulverized-coal flame or a small furnace in which the attainment of high temperature was desired, rather than high thermal efficiency, together with a comparatively high cost for oil or gas. The existing types of steam boilers had small furnaces set closely under the boilers. The destructive action of the flame on refractory and boiler surfaces and frequent failure to obtain satisfactory thermal efficien-

. [7] Gadd, C. J., *J. Franklin Inst.*, **182**, 823–52 (1916). Longnecker, C., *Iron Age*, **102**, 619–23 (1918). Mathewson, E. P., and Wotherspoon, W. L., *Trans. Can. Mining Inst.*, **22**, 33–59 (1919). Bean, W. R., *Proc. Tenth Fuel Eng. Meeting, Appalachian Coals, Inc.*, **2**, 268–73 (1935). Campbell, C., *Colliery Guardian*, **151**, 907–8 (1935). Herington, C. F., *Iron Age*, **143**, No. 3, 27–9, 57 (1939), **143**, No. 5, 48–50, 84 (1939).

[8] Bender, L. V., *Trans. Am. Inst. Mining Met. Engrs.*, **51**, 743–51 (1915). Browne, D. H., *ibid.*,

51, 752–63 (1915). Kuzell, C. R., *Eng. Mining J.*, **101**, 302–6 (1916).

[9] Engdahl, R. B., *Iron Age*, **150**, No. 27, 27–31 (1942). Engdahl, R. B., and Graves, F. E., *Trans. Am. Soc. Mech. Engrs.*, **65**, 31–45 (1943). Anon., *Pulverized Coal for Metallurgical Furnaces*, Babcock and Wilcox Company, New York, 1942, 12 pp.

[10] Blizard, J., *U. S. Bur. Mines, Bull.* **217** (1923), 127 pp.

cies condemned applications to steam boilers to mediocre success.

About 1917, John Anderson of the Milwaukee Electric Railway and Light Company started experiments on a 468-horse-power Edgemoor boiler. Careful tests on

FIG. 2. Section through furnace, Oneida Street Station, Milwaukee.[11]

this unit led to the design of the Lakeside station which was placed in service and tested in 1921. Aside from their outstanding success, these installations were unique because: (1) considerable money was invested in furnaces which seemed best suited to the purpose; (2) the units were fully and carefully tested; and (3), probably most important of all, the test data and operating experiences were published.[10, 11]

The first installation at the Oneida Street Station, Fig. 2, was a refractory furnace with high-velocity jet burners set in the front arch. In order to protect the ledge

[11] Kreisinger, H, and Blizard, J., *Mech. Eng.*, **43**, 321–2, 326 (1921) ; *Ind. Eng. Chem*, **15**, 249–51 (1923). Kreisinger, H, Blizard, J., Augustine, C. E., and Cross, B. J , *U. S. Bur. Mines, Bull.* **223** (1923), 92 pp., **237** (1925), 77 pp.

below the burners, a water-cooling coil was placed across the bottom of the furnace. There was still some erosion on the back wall, but it was not considered advisable to extend the water-cooled area for fear of causing unstable ignition.

Air-cooled refractory walls were used in the furnaces of the Lakeside Station, Fig. 3. It was expected that the air-cooling would stop slagging and erosion of refractory.

The Milwaukee experiences proved that pulverized coal could be burned at efficiencies unattainable, at that time, in any other way. It was hoped that pulverized coal would combine the flexibility and ease of

FIG. 3 Section through furnace, Lakeside Station, Milwaukee.[11]

control of oil or gas with the low cost of coal. It soon became apparent that the control could be obtained but that the range was limited. At low ratings, ignition was likely to be unstable. At higher ratings incomplete combustion, erosion, and accumulations of ash combined to limit the

economical range of operation. The wide publicity and thorough study given to these difficulties led to rapid development.
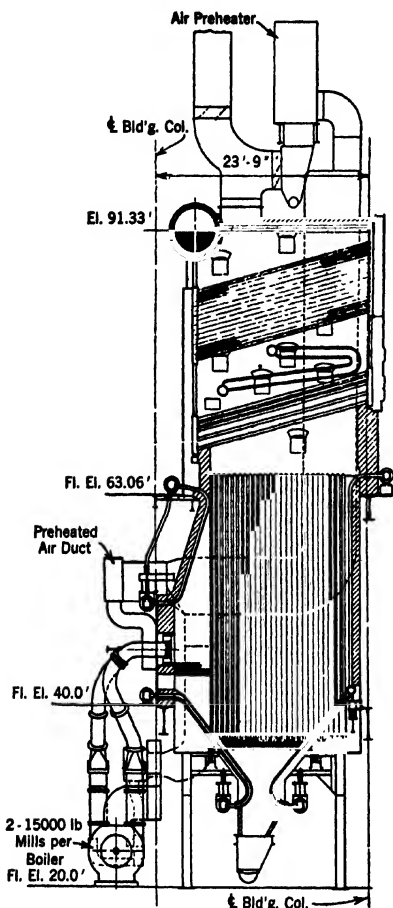
However, this development was cautiously based on small changes from existing types of proved success.

The Cahokia Station of the Union Electric Light and Power Company has prob-

ably seen more of the evolution of modern pulverized-coal-fired boilers than any other single station.[12] The first four installations were similar to those at Lakeside except for increasing amounts of water-cooled wall surface. The unit placed in operation in October 1927, Fig. 4, marked the close of one phase of development. The furnace was almost completely water-cooled. The much-feared unstable ignition was prevented by a combination of several factors. The cooling effect of the walls was compensated by a rise in average temperature due to lower excess air. The lower excess air was permissible on account of a different burner design in which the coal, together with all the air needed for combustion, was mixed, given a whirling motion, and blown into the furnace through the front wall. Ignition and intense combustion were held close to the burners. The early and intense mixing assured complete combustion with the reduced air supply.

The limitations of water-cooled walls were shown by an installation at Buffalo, N. Y., Fig. 5.[13] Owing to special conditions, this unit was designed for high rates of heat release per unit volume, although at some sacrifice in efficiency. The burners were set in the walls of an 8-foot square well so as to give a powerful whirling motion. The intense mixing, produced by centrifugal action, apparently increased the rate of heat release until bare wall tubes were blistered and refractory or iron-protecting blocks suffered rapid erosion. Possibly adequate circulation of pure water might have prevented tube damage, but it

[12] Tenney, E. H., *Trans. Am. Soc. Mech. Engrs.*, 49–50, FSP 50–71, 177–85 (1927–8); *Mech. Eng.*, 50, 767–73 (1928); *Proc. 3rd Intern. Conf. Bituminous Coal*, 2, 370–99 (1931).

[13] Cushing, H. M., and Moore, R. P., *Trans. Am. Soc. Mech. Engrs.*, 49–50, FSP 50–10, 63–74 (1927–8).
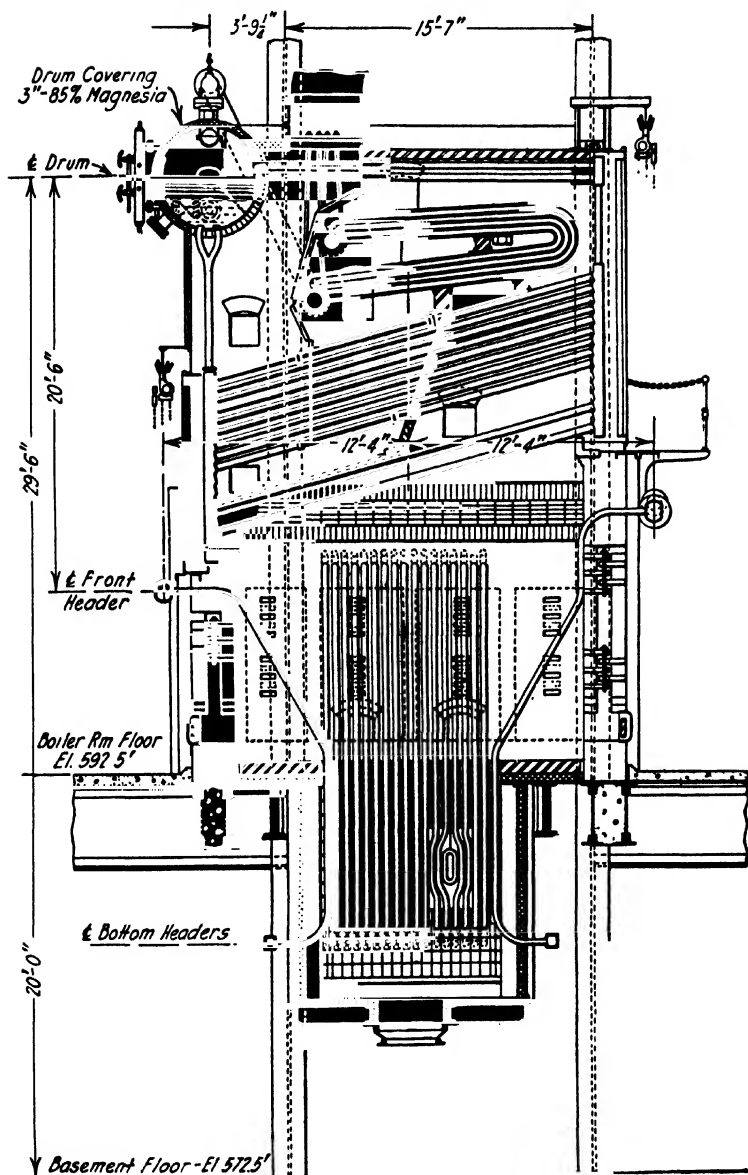
FIG. 5. Well-type furnace.[12]

was indicated that even water-cooled walls could be damaged by extreme flame impingement.

On the basis of the experience with the first installation, three furnaces were installed which had somewhat larger wells.

The wall tubes were protected by smooth refractory-coated iron blocks. With less confinement, erosion was greatly reduced, but the temperatures were still high enough to cause molten ash to collect in the bottom of the well. When first encountered
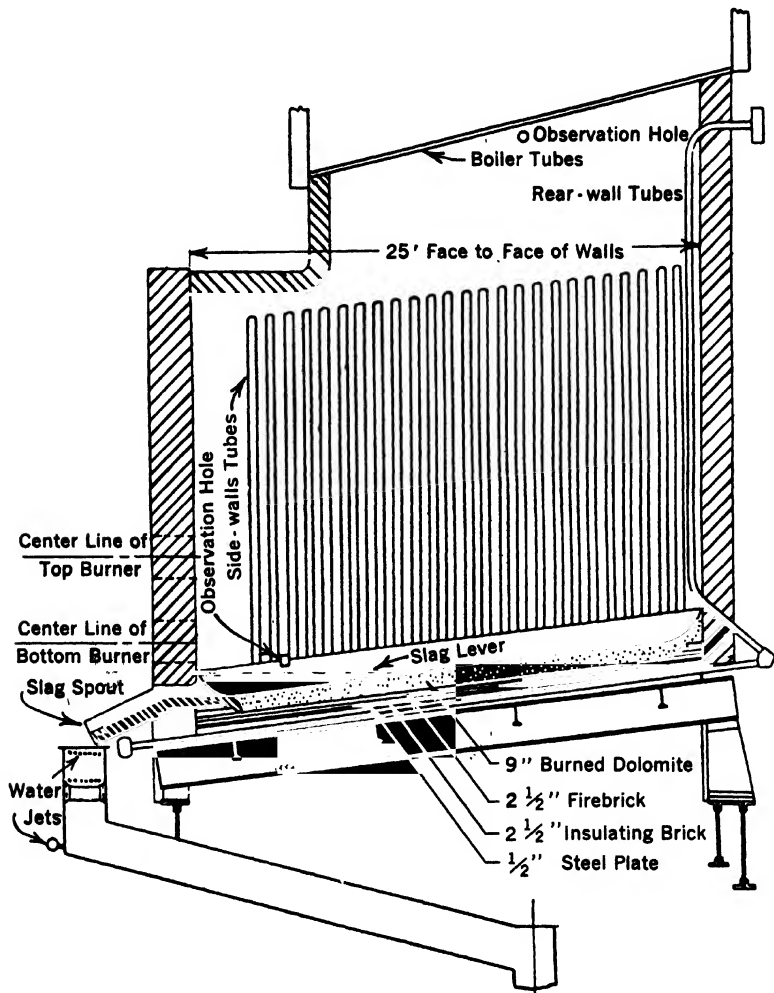
Fig. 6. Experimental slag bottom furnace.[16]

with the small well furnace,[14] the molten ash presented a difficult problem. After a few trials it was found that the molten ash could be handled, even more easily than the dry, pulverulent ash, by allowing it to flow into jets of water breaking it into a granular product.

This was the first successful application of the slagging-type furnace, but the idea was neither new nor without an industrial background. As early as 1873, Crampton [15] suggested the use of pulverized coal under steam boilers under such conditions that the ash would collect and could be intermittently tapped off in the molten form. The metallurgical industries had handled slags of similar composition for many years. The idea had been tried but given up as impractical until it was found to be the necessary and fully practical result of the use of an unusual type of furnace.

In 1928, a more conventional type of furnace, Fig. 6, was modified for use as a slag-tap furnace. The slag from a bituminous coal having an ash-softening temperature of 2,700° F could not be tapped; that from a bituminous coal having an ash-softening temperature of 2,470° F was on the border line.[16] This limit was characteristic of the individual furnace. The tap hole was not located in the most advantageous position. The slag pool was close under the burners but was cooled by radiation to bare wall and boiler tubes.

Modern steam boiler furnaces using pulverized coal have evolved from the types already discussed. The principal problems have been the disposal of ash and the production of steam at a predetermined pressure and superheat temperature at varied steaming rates.

Figure 7 shows an open-pass type boiler with superheater, economizer, and air heater. The entire furnace is water-cooled. The jet burners are directed towards the bottom of the primary furnace. Temperatures are such that the ash is molten in the primary furnace and first open pass. The walls are covered by an equilibrium slag layer, the excess flowing continuously into the bottom of the furnace. In the second open pass, the downward flow helps prevent ash accumulations, although temperatures are such that the ash is in a sticky condition. In the final pass, the ash is dry and either falls into the ash hopper or is carried up the stack. The rate of heat absorption, and, therefore, the temperature of the gas reaching the superheater, depend upon the state of accumulation of ash. In order to control the superheat temperature the final pass is split into two parallel sections: one contains only economizer coils; the other contains the superheater and the remainder of the economizer. The steam temperature is controlled by dampers regulating the proportions of gas flowing through the two sections.

Figure 8 shows a twin furnace in which the dimensions are such that the ratio of wall area to volume is greater than in most conventional designs. This provides adequate cooling to prevent slagging of the closely spaced convection heating surfaces. The superheater, partly radiation and partly convection, is placed in one furnace only so that constant steam temperature can be maintained over a wide range of operation by varying the fuel ratio to the two furnaces.

The furnace shown in Fig. 9 has a forced circulation boiler, a novelty in American central-station practice. High-velocity jet burners are placed in each corner and directed towards the center of the furnace in such a way as to produce a powerful whirl-

[14] Cushing, H. M., *ibid.*, **51**, 263–70 (1929).

[15] Crampton, T. R., ref. 2.

[16] Sherman, R. A., Nicholls, P., and Taylor, E., *Trans. Am. Soc. Mech. Engrs.*, **51**, 399–410 (1929).
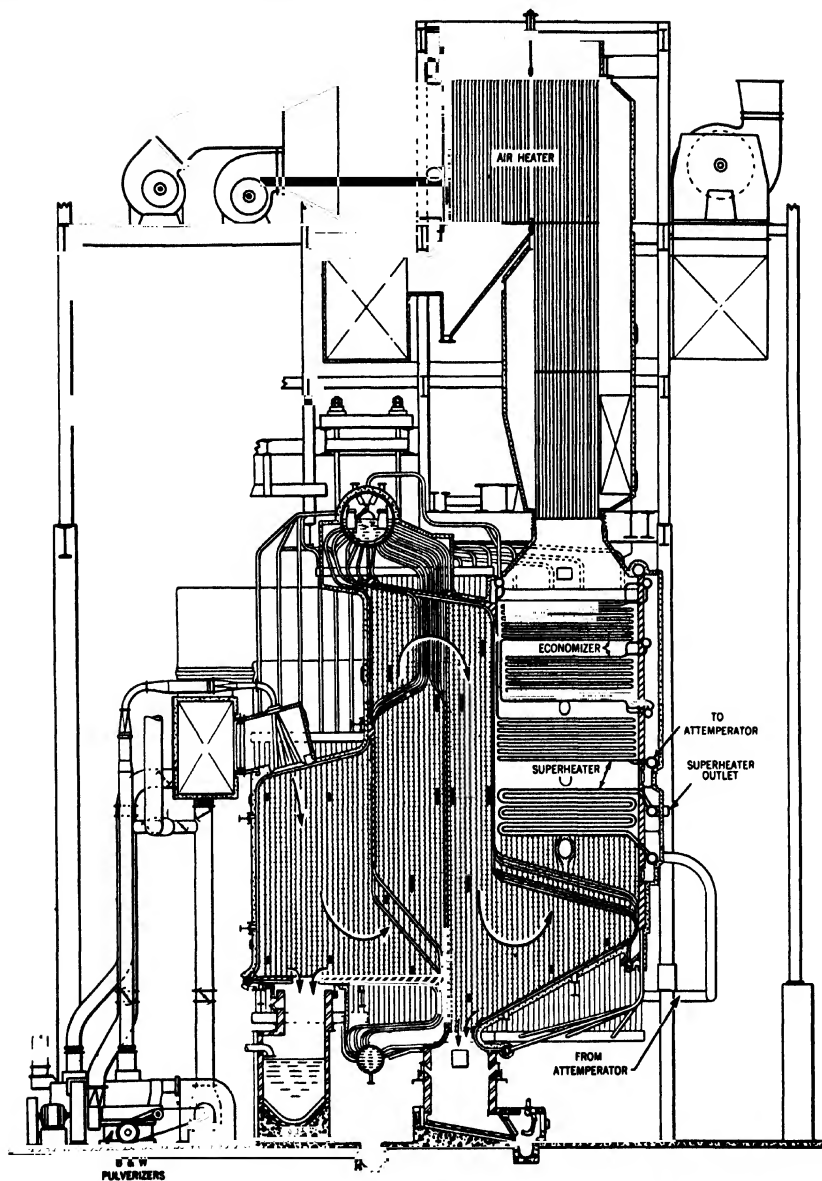
FIG. 7. Boiler unit with open-pass furnace. (Courtesy of the Babcock & Wilcox Company.)
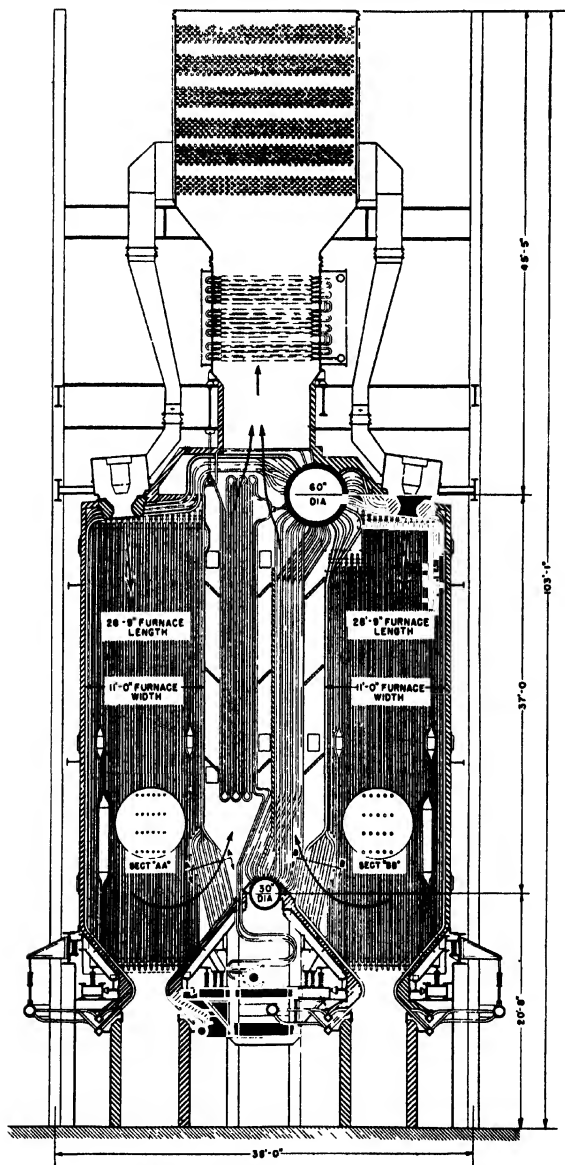
FIG. 8. Boiler unit with twin furnace. (Courtesy of the Foster-Wheeler Corporation.)

El. 186′ - 3″

El. 174′ - 0 ½″

El. 165′ - 0″

El. 153′ - 6″

El. 137′ - 0″

El. 137′ - 0″

El. 118′ - 0″
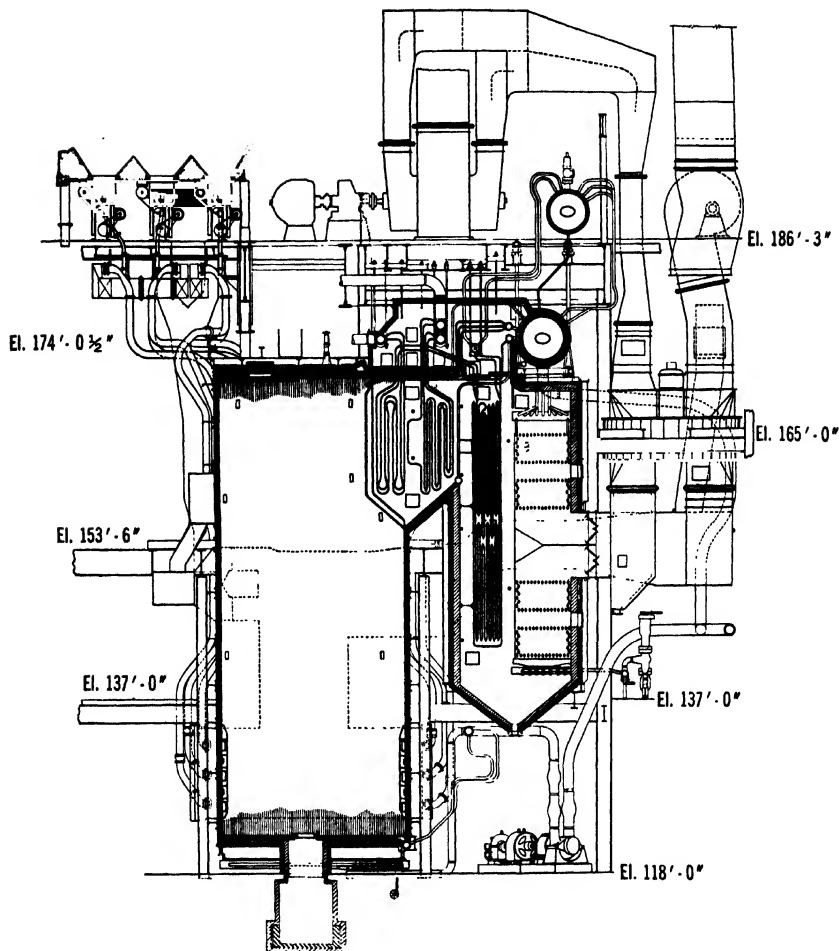
Fig. 9.   Forced circulation boiler, tangentially fired, auxiliary oil burners.   (Courtesy of the Combustion Engineering Company.)

ing motion. The flame fills the bottom of the furnace, keeping the temperature on the floor high enough to slag the ash even from high-ash-fusion-temperature coals. Steam temperature is controlled by by-passing the final section of the superheater.

AUXILIARY EQUIPMENT AND BURNERS

At about the same time that the slag-tap furnace was being developed, there was a general change in the equipment for pre-paring pulverized coal. Early boiler-plant installations closely followed the practice in

the cement and metallurgical industries. The demand for reliability dictated the use of the bin and feeder system with its high capital and operating costs for coal driers, cyclone dust separators, conveying equipment, and coal feeders. These costs were justified as long as they were less than the probable losses due to outages and decreased flexibility in the direct-fired system.[17] The two systems as applied to the

17 Grunert, A. E., *ibid.*, **53**, FSP 53-4, 35-48 (1931).

same boiler are shown in Figs. 10 and 11. In the direct system, the coal flows by gravity from the bunker into the pulverizer and the pulverized coal is swept out and carried into the furnace by means of the primary air. The coal drier is eliminated. Drying is accomplished in the pulverizer by heating the primary air to such a temperature that the air leaving the pulverizer is above the dew point.

Typical pulverizers adapted to direct-
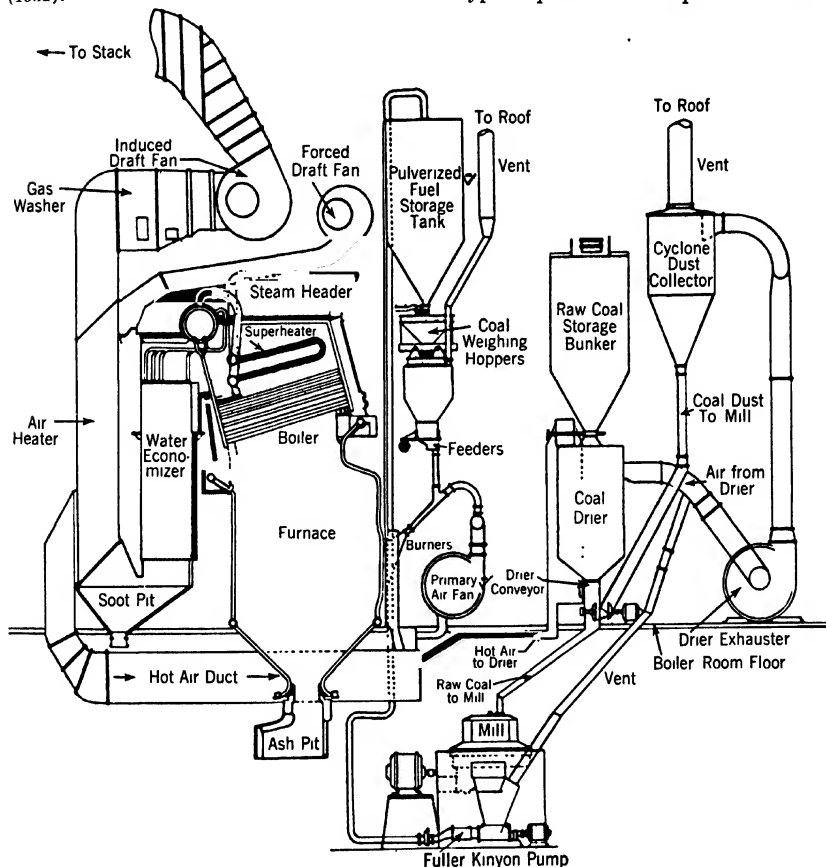
Fig. 10. Furnace with bin and feeder system.[17]
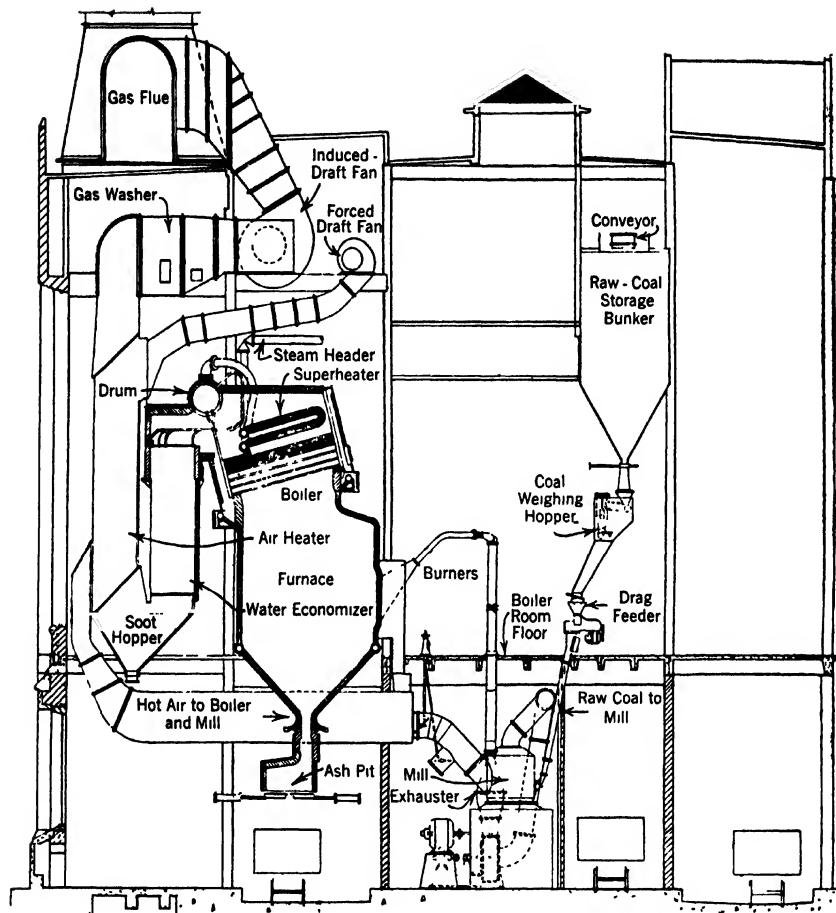
FIG. 11. Furnace with direct-fired system.[17]

fired systems are shown in Figs. 12, 13, and 14. Air classification has generally replaced screens for rejecting coarse material to be reground. Such screens are often the cause of outages. The bearing surfaces are protected from coal dust and are lubricated while in operation. The grinding elements are massive and can stand considerable wear before replacement is necessary.

Placing the primary air fan ahead of the pulverizer eliminates fan wear due to abrasion by coal.

Along with the development in pulverizers there has been a steady development in the design of burners. The simplest burner is merely a pipe introduced into a hole in the wall of a furnace. Others vary from changes in cross section of the end of
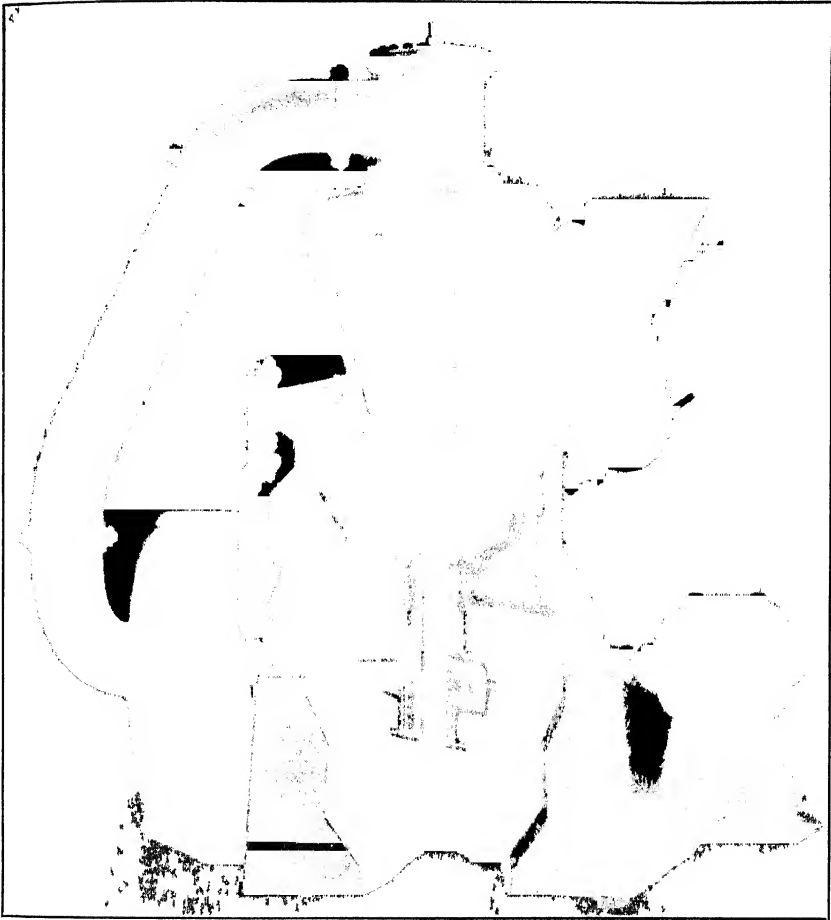
Fig 12   Raymond bowl mill   (Courtesy of the Combustion Engineering Company)

the pipe to complicated arrangements of pipes, chambers, and nozzles   Their essential function is to introduce coal and air into the furnace under such conditions that stable flames can be maintained with minimum danger of flashbacks into coal-supplying equipment or piping   Their performance depends not only on the burner but also on the furnace and on the conditions in the approach piping   What happens in the burner, before heating and ignition processes begin, is of no importance except as it influences gas velocities and the concentration and velocity distribution of coal particles

Most of the burners in cement kilns, and many of those in the larger metallurgical and steam-boiler installations, are high-ve-
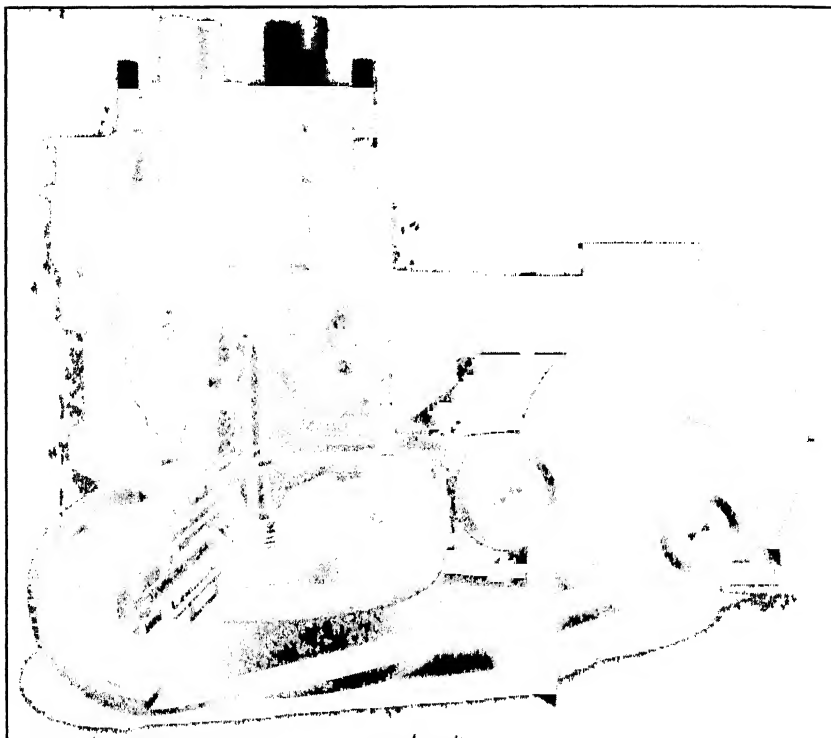
FIG 13   Babcock & Wilcox type E pulverizer   (Courtesy of the Babcock & Wilcox Company)

locity jets blowing the coal, suspended in part or all of the air needed for combustion, into a long flame In order to obtain high ratings with such burners it is necessary to provide either for extremely long flames or for a large number of small burners with complicated systems of approach piping

Various devices have been used to obtain high capacities in short flames Such burners generally rely on impingement of opposing gas streams to bring about turbulence   The types in most common use [18]

[18] Kreisinger, H and Caracristi, V Z , *Mech Eng* , **64**, 365–8 (1942)

pass the coal and primary air through a central tube and the secondary air through a surrounding annulus   The flow patterns in the burner are such as to give these gas streams opposing rotations, and sometimes vanes break them into a number of smaller streams   Ignition occurs in the primary air stream before mixing with the secondary air

PULVERIZED COAL IN SMALL FURNACES

The more successful applications of pulverized coal have been in large furnaces where ample space is available for complete combustion without impingement of

FIG 14. Double-classifier ball mill (Courtesy of the Foster Wheeler Corporation)

flames on furnace walls. Since 1930 most installations of large steam boiler furnaces have been fired with pulverized coal. There has been a tendency to develop standardized types of small boilers which can be fired with pulverized coal, oil, or gas, as illustrated by Fig. 15, but on units of less than 25,000 to 30,000 pounds of steam per hour most coal-fired units are stokers.[19]

[19] Rosencrants, F. H., *Combustion*, **9**, No. 10, 31–6 (1938).

There have been many attempts to apply pulverized coal to standard types of steam locomotives.[20] The most extensive tests have been made in Germany, where high fuel costs and the scarcity of oil have

[20] Muhlfeld, J. E., *Trans. Am. Soc. Mech. Engrs.*, **38**, 1043–83 (1916). Kleinow, B. W., *Proc. 2nd Intern. Conf. Bituminous Coal*, **1**, 792–816 (1928). Roosen, R. O., *Trans. Am. Soc. Mech. Engrs.*, **52**, RR-52-8, 97–107 (1930) ; *Proc. 3rd Intern. Conf. Bituminous Coal*, **2**, 85–106 (1931).
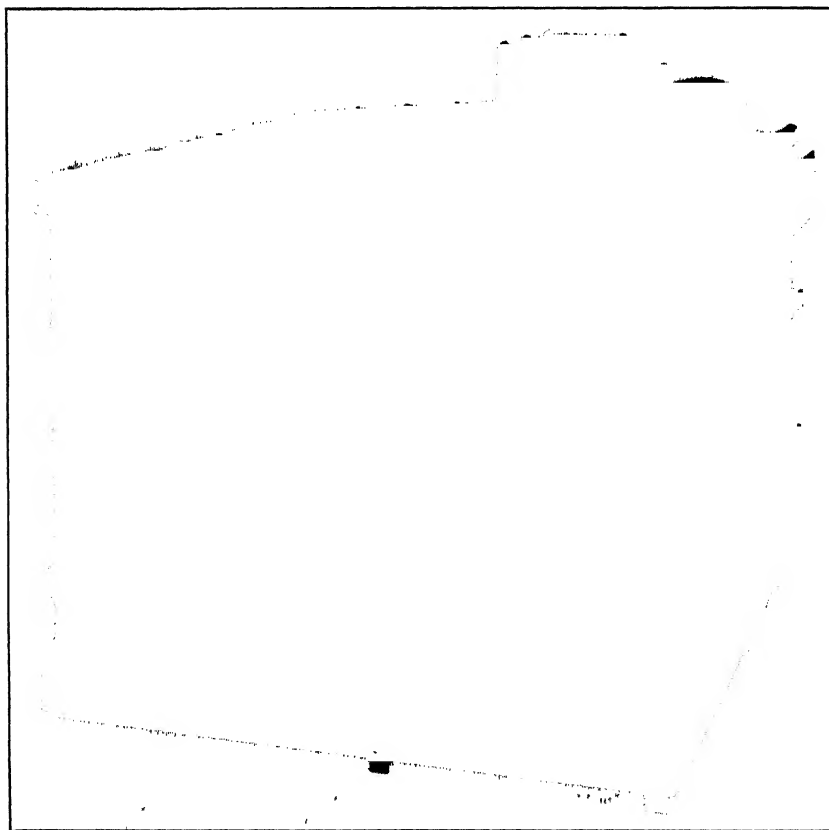
Fig. 15.   Standardized small boiler unit adapted to firing of pulverized coal, oil, or gas.   (Courtesy of the Combustion Engineering Company.)

given impetus to developments for more economical use of coal. The low cost of bituminous coal, the ease of burning oil, and the adaptability of the Diesel engine to railroad practice have limited such developments in this country. Large-scale use of pulverized coal will probably depend upon the development of new types of locomotives combining the economies of central-station practice with the limited dimensions available in railroad practice.

RAW COAL DUST AND COMBINATION FIRING

With coals that produce large quantities of fine slack, particularly the German brown coals, it is possible to dispense with part or all of the pulverization equipment.[21] In Krämer mill firing, a hammer mill is set at the bottom of a deep shaft alongside the furnace. Drying is accomplished in the shaft. Fine particles are blown directly into the furnace without reaching the mill. Sometimes screens have been provided to keep the coarser particles from being blown into the furnace.

In raw-coal-dust firing the combustion of large particles is completed on a pinhole grate. This is really a spreader stoker in which most of the combustion is completed while the coal is in suspension. In so far as that part of the combustion which occurs in suspension is concerned, the performance of a spreader stoker is a continuous extension of the pulverized-coal furnace. The percentage of the total combustion which is completed in suspension may be varied within wide limits. It is necessary, however, to take into account the particle-size distribution and the environment of the individual burning particles. There appears to be some loss due

to medium-sized particles light enough to be carried in the gas stream and yet so large that combustion is not completed in the furnace.

Combination firing of pulverized coal with oil or gas has often been used. Sometimes the combination has been an expedient to increase capacity or to avoid operating difficulties; more often it has been to use a fuel available in economic but inadequate quantities or to avoid a shutdown due to temporary shortages of coal. Some installations indicate that such combinations are fully practical.[22] A furnace suited to the use of pulverized coal generally has ample combustion space for oil or gas but it may not be able to operate at full capacity with these fuels. Furnaces having large areas of radiant heating surfaces may be extremely sensitive to radiation characteristics of the different flames.

FUELS ADAPTED TO FIRING IN SUSPENSION

Any carbonaceous material, capable of being reduced to a powder, is a conceivable pulverized fuel. The entire range of coal and coallike substances from pitch [23] to anthracite [24] has been used. Aside from pulverization, the main problem, with any given fuel, is to obtain stable flames and prevent coke deposits in the burners.

Anthracite must be fired with minimum primary air and maximum fineness. Fine pulverization also aids in obtaining complete combustion in furnaces of reasonable size. Pulverized pitch can be burned with ease, but care must be taken to prevent flashbacks and to avoid impingement of

[21] Schulte, F., *Z. Ver. deut. Ing.*, **80**, 1237–42 (1936). Schöning, W., *Arch. Wärmewirt.*, **20**, 307–9 (1939).

[22] Anon., *Power*, **85**, 564–8 (1941) ; *Power Plant Eng.*, **46**, 52–3 (1942).

[23] Davies, E. B., *J. Inst. Fuel*, **12**, 243–7 (1939). Clarke, E. W., *Trans. Am. Soc. Mech. Engrs.*, **61**, 577–9 (1939).

[24] Mayer, J., *J. Inst. Fuel*, **11**, 305–26 (1938). Frick, C. H., *Trans. Am. Soc. Mech. Engrs.*, **64**, 257–61 (1942).

unignited particles on hot surfaces. Surfaces, such as diffuser vanes, which are exposed to radiation without adequate cooling are likely places for coke formation. The use of low-rank coals of high moisture content is principally an economy confined to those localities where transportation costs are heavily in its favor.

If a given fuel is available in reliable quantities at a price such as to make it economical to install the necessary equipment, it is generally possible to use that fuel. Although a given installation may be quite sensitive as to the kind of coal it can use and maintain capacity and efficiency, it is often possible, at a moderate cost, to adapt the equipment to a wide variety of fuels.

THE PULVERIZED-COAL ENGINE

It is possible to burn pulverized coal in an internal-combustion engine.[25] Unlike Diesel oil, the coal cannot be injected but must be aspirated or blown into the engine. The coal is first introduced, together with a limited supply of air, into a precombustion chamber from which it passes through an orifice and mixes with the remainder of the combustion air in the cylinder. Otherwise the engine is similar to an ordinary slow-speed Diesel engine. In fact, Diesel engines have been converted to burning pulverized coal by adding the necessary precombustion chamber and valve gear.

Economic development of the pulverized-

25 Pawlikowski, R., *Proc. 2nd Intern. Conf. Bituminous Coal*, 1, 768–91 (1928); *Proc. 3rd Intern. Conf. Bituminous Coal*, 2, 317–48 (1931). Schulte, F., and Litterscheidt, W., *Gluckauf*, 70, 1189–94, 1222–7 (1934). Dept. Sci. Ind. Research (Brit.), Fuel Research Board, *Rept. Year Ended 31st March 1938*, 255 pp., pp. 220–4. *Rept. Year Ended 31st March 1939*, 205 pp., pp. 182–3. Wahl, H., *Wärme*, 65, 159–65 (1942), as reported in Dept. Sci. Ind. Research (Brit.), Fuel Research Board, Intelligence Sec., July 18, 1942.

coal engine would have to overcome several major difficulties. Extremely fine pulverization is necessary to obtain the burning speeds required even in slow-speed engines. The pulverized coal, as well as the ash, has an abrasive action on valves, cylinder walls, piston rings, etc. These difficulties are such that it appears more economical to use Diesel oil, even though the oil is obtained by hydrogenation of coal.

CONDITIONS IN PULVERIZED-COAL FURNACES

Few data are available on conditions within pulverized-coal flames. Although furnace-wall temperatures have occasionally been stated or could be inferred from the nature of the application, data on temperatures within the pulverized-coal flame are scarce and often of questionable quality. Flue-gas compositions are often the basis of furnace control. Gas compositions within the furnace have rarely been reported. The information that is available is confined mainly to units in which high excess air, low firing rates, or other causes tended to reduce the temperature.

In connection with the 1920 tests at the Oneida Street Station, a temperature survey was made.[10, 11] A maximum, over 2,700° F, was found just off the ledge at the bottom of the furnace. Mixing of secondary air with the long flames from burners set in the front arch was probably slow until the disturbing effect of the ledge and the sharp change in direction of gas flow brought about thorough mixing and intense combustion.

The prevalence of slag deposits and refractory erosion by molten slag indicates that the burning coal particles must reach temperatures above the ash-fusion temperature. In an attempt to explain the striking difference in refractory service conditions in two similar furnaces both us-

ing similar low-ash-fusion coals, a careful study was made of the conditions within these furnaces at various rates of firing.[26] A typical set of data is shown in Fig. 16. A complete survey was not made. Sampling points were selected along what was estimated to be a stream line passing through the heart of the flame. The min-

had some effect on furnace temperatures but was probably less important than the high excess air. The high oxygen concentration above the front arch may be indicative of leaks in the setting, but it is probable that some secondary air penetrated between the coal flames. The low carbon monoxide concentrations, generally
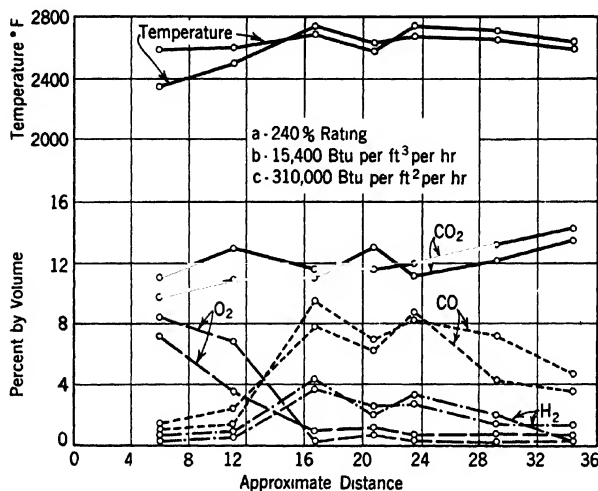
FIG. 16. Gas temperature and composition in furnace burning pulverized Illinois coal.[26]

ima in temperature, carbon monoxide, and hydrogen indicate that the fourth sampling point was not properly located. The rate of combustion was apparently limited by the rate of mixing of secondary air. From a maximum at 16 feet from the burners, the carbon monoxide and hydrogen were slowly reduced in concentration, while the oxygen remained below 1 percent.

The data shown in Fig. 17 are for a furnace similar to that of Fig. 16 except that the side, as well as the back, walls were water-cooled.[27] The increased cold wall

less than 0.75 percent, indicated comparatively rapid mixing of coal and air.

Figure 18 shows the same data for a furnace with almost completely water-cooled walls and with all the air needed for combustion admitted through the burners set in the front wall. Under these conditions combustion was much more intense; the concentration of carbon monoxide was even further reduced; and it was possible to operate with much less excess air at a small gain in thermal efficiency. The distribution of oxygen concentrations indicates either that the mixing of primary and sec-

26 Sherman, R. A., and Taylor, E., *Trans. Am. Soc. Mech. Engrs.*, **49–50**, FSP 50–38, 125–40 (1927–28).

27 Tenney, E. H., *Proc. 3rd Intern. Conf. Bituminous Coal*, **2**, 370–99 (1931).
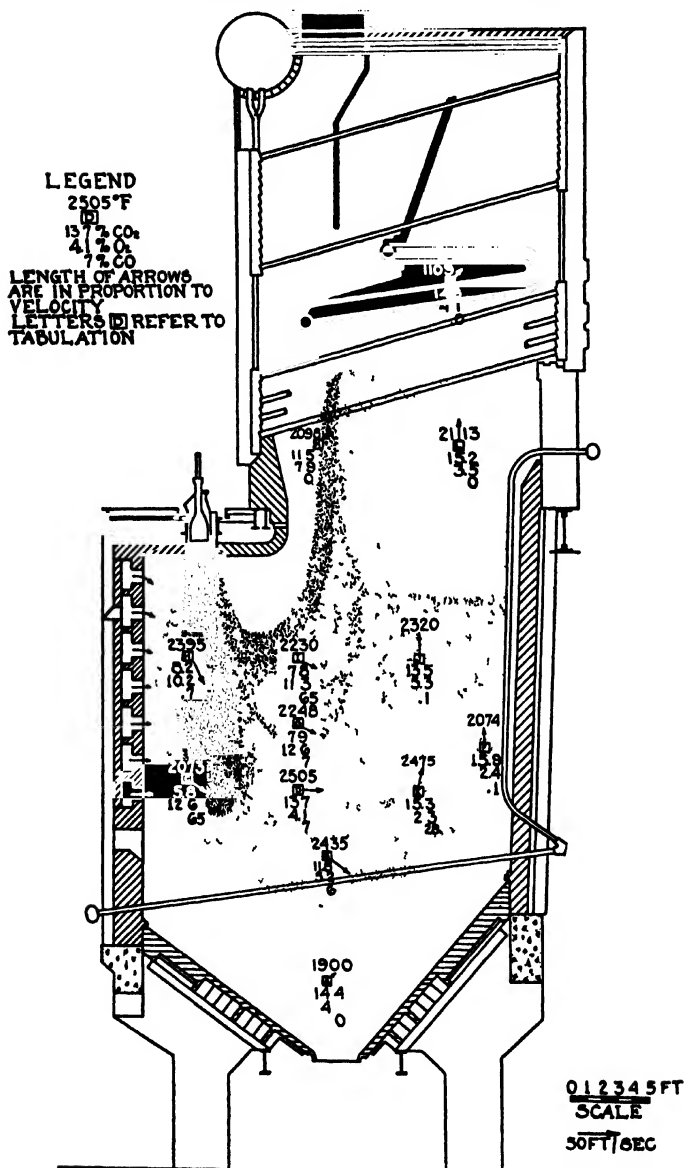
Fig 17   Temperature and gas composition in furnace with vertical firing [37]
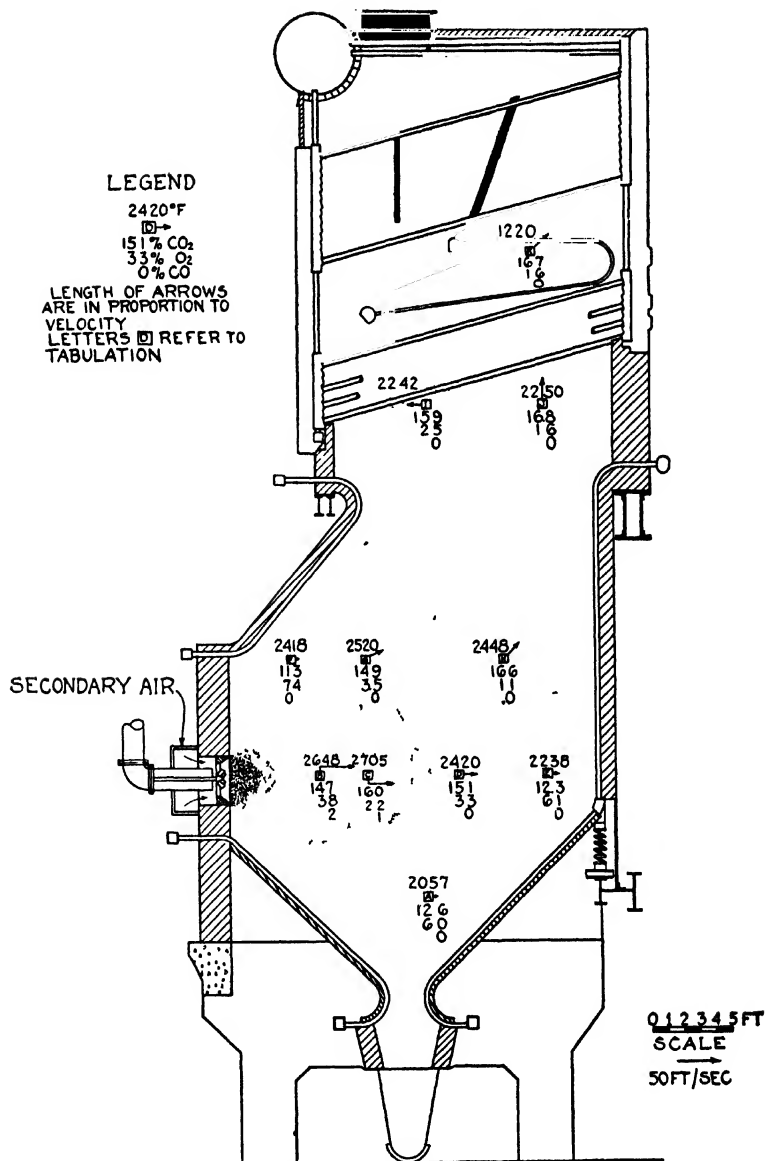
FIG 18   Temperature and gas composition in furnace with short turbulent flame [27]

ondary air was not complete or that the air currents diverged more rapidly than the coal dust.

The influence of water-cooled walls on the combustion process has been the subject of considerable speculation but very little experimentation. The average cooling effect may be compensated by increased firing rates and by decreased excess air. The formation of high-temperature gradients cannot be avoided. They are a necessary consequence of heat absorption in the furnace. Temperature measurements in several furnaces at the Sherman Creek Station [28] showed that the furnace temperature was relatively uniform across the furnace except for a sharp drop within about 6–12 inches from the cold wall.

One of the most comprehensive studies of furnace conditions was that reported by Schwiedessen.[29] Measurements of gas velocities, temperatures, gas compositions, and dust loadings were given. Proximate analyses were made on the dust. Dust samples were sized by elutriation and photographed. Unfortunately this study was confined to a peculiar installation in a metallurgical heating furnace and no information was given on the influence of different fuels and rates of firing.

Commercial furnaces generally are not suited to the insertion of thermocouples and sampling probes into the furnace cavity. In the surveys reported by Sherman [30] this difficulty was avoided by the use of a special testing furnace. Any lack of similarity between the test furnace and commercial installations was compensated

by the ease with which the individual factors could be studied.

The furnace cavity was a cylinder 14 feet long and 3.5 feet in diameter with the burner set in the front wall and directed along the axis. The burner was formed by a venturi throat opening into an annulus 7 inches in outside and 4 inches in inside diameter. Care was taken to make the furnace air-tight so that all the air entered through the burner.

Sherman's data included gas velocities, gas analyses, temperatures, radiation densities, and percentages of unburned carbon as determined from dust samples. The velocity and gas-composition data indicated that the flame did not fill the cross section of the furnace until about 10 feet from the burner. An annular eddy filled the space between the flame cone and the front wall. Thermal expansion of the entering gases caused strong accelerations, in one test from 40 to 90 feet per second per second within 1 foot from the burner. There was no evidence of turbulence. The influence of the annulus on the velocity distribution persisted for about 2 feet.

Ignition and combustion were rapid. Figure 19 shows the temperature and unburned carbon plotted against time, measured from the time of entrance into the furnace, for four coals. These coals were pulverized to approximately the same percentage on 200-mesh and fired at similar rates. The striking differences in the burning rates were characteristic of the individual coals but could not be evaluated in terms of coal properties. The lowest-volatile coal showed the lowest burning rate, but the remaining coals showed differences which could not be explained on the basis of volatile contents.

No single criterion for fineness was found which would explain the results, except that, for a given percentage through 200

28 Sherman, R. A., *Mech. Eng.*, **49**, 335–8 (1927).

29 Schwiedessen, H., *Arch. Eisenhüttenw.*, **5**, 291–8 (1931–2).

30 Sherman, R. A., *Proc. 3rd Intern. Conf. Bituminous Coal*, **2**, 510–51 (1931); *Trans. Am. Soc. Mech. Engrs.*, **56**, 401–9 (1934).

mesh, the percentage through 100 mesh was markedly significant. The coal was pulverized in a conical ball mill, and the product passed through a special air classifier. The ability to obtain low unburned

range of temperatures available was small, but a significant decrease in the percentage of carbon at a given point with increasing furnace temperature was found. An increase of burning rate with furnace tem-
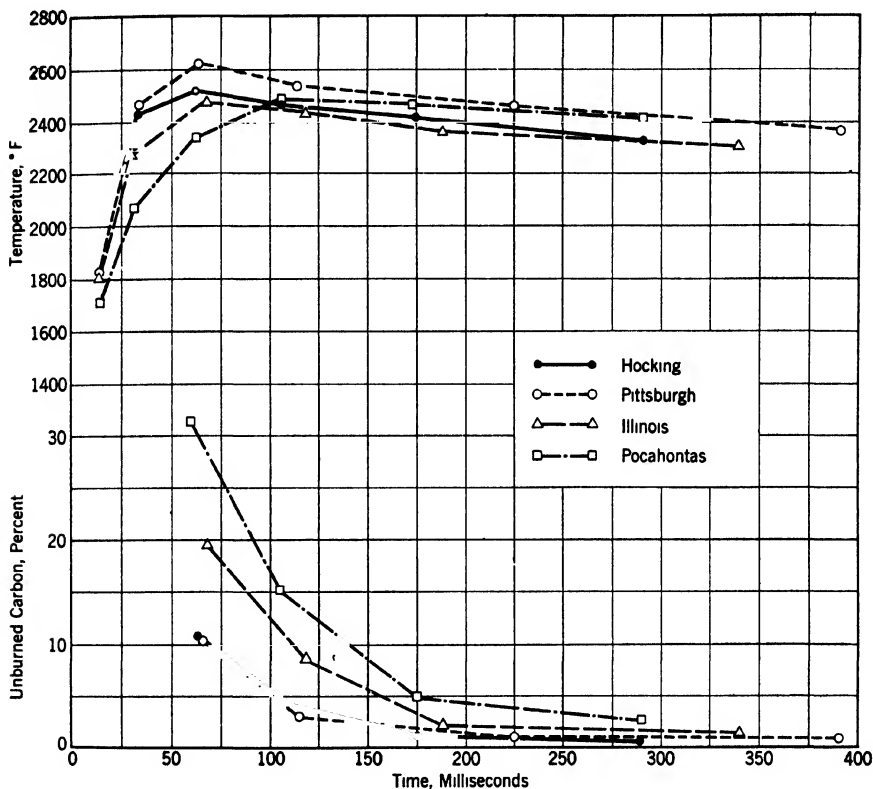
Fıɢ. 19.   Temperature and unburned carbon for four coals in an experimental furnace.[80]

carbon losses without turbulence and with such a short flame was probably a result of the comparatively low percentage of coarse coal.

It was impossible to study the effect of furnace temperature except by taking samples at various times after starting the furnace and before the refractory walls had reached their equilibrium temperature. The

perature was a possible explanation, but the results could be equally well explained on the basis of a shift of the flame due to earlier ignition in the hotter furnace.

Measurements made by means of a total radiation thermopile showed some dependence upon the coal. Using a given coal there was little or no dependence of the emissivity upon rate of firing, excess air,

or coal fineness. These factors generally affected the temperature in the expected manner, but the radiation also changed in such a way as to minimize the variation in emissivity.

The emissivity depended strongly upon the position along the flame, ranging from about 0.7 to 0.3. As a result of the falling emissivity the radiation generally reached a maximum before the maximum temperature was reached. It is probable that the emissivity was mainly dependent upon the degree of completion of the combustion process. The failure to find increasing emissivity with increasing fineness may have resulted because the comparison was made at equal times rather than at equal degrees of combustion.

The gas analyses showed a small concentration of carbon monoxide, generally less than 1 percent when burning coal in excess air, but none when burning coke. This was interpreted as indicating that the large concentrations of carbon monoxide found in some installations are due to a deficiency of air. The failure to find carbon monoxide with coke led to the conclusion that the small concentrations found with coal were due to the volatile matter.

Bailey [31] has reported temperatures in furnaces of the slag-tap type. The temperatures were measured on either side of slag screens which divided the furnaces into two or more cavities. On the assumption that the theoretical heat was all released in the primary furnace cavity, these temperatures were used to calculate the rates of heat absorption in the various parts of the furnaces. The temperatures, applying to the primary furnace cavities, are plotted against the rate of heat absorption per square foot of primary furnace wall in Fig. 20. The adiabatic temperature is that

31 Bailey, E. G., *ibid.*, **61**, 561–9 (1939).

which would have been attained had combustion been completed without loss of heat. The furnace temperature was measured at the outlet of the primary furnace cavity. This appears to have been the first point at which reliable temperature measurements could be made.

The Stefan-Boltzmann law was used to calculate an equivalent heat-receiving sur-
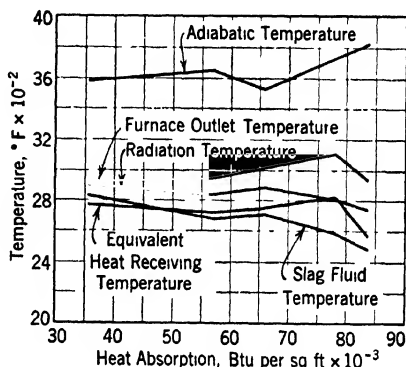
FIG. 20. Temperatures in slagging primary furnaces.

face-temperature on the basis of the arbitrary assumption that furnace outlet temperature, as the effective radiation temperature of the heat source, would account for the rate of heat absorption by the furnace walls. The receiving temperature was found to correspond approximately to the slag fluid temperature. There appears to be a systematic deviation as the rate of absorption increases, but the check is remarkably good in view of the assumptions.

Temperature and gas composition data must be carefully interpreted. Thermocouples are more or less slow to react to changes in temperature. Since the time of passage of coal particles through the furnace is generally of the order of a few seconds or less, the indicated temperature must be a time average over a period dur-

ing which many particles pass near the couple, and in some cases over changes of a larger scale due to fluctuations of the flame.

Similar considerations apply to samples for gas analysis. A definite composition will exist in a sufficiently small volume, but, as the size of sample is decreased, difficulties will arise both in the technique of sampling and analysis and in the determination of the environment from which the sample was taken. This places serious limitations on the usefulness of gas-analysis data for a study of the mechanism of combustion. The absence of appreciable amounts of carbon monoxide does not preclude the presence of considerable concentrations near the surface of burning particles. Conversely, the presence of oxygen need not indicate the presence of appreciable concentrations near the surface of a burning particle.

Ignition

The phenomenon of ignition is so common and yet has so many variable aspects that the subject must be given careful consideration. Ignition may occur in any exothermic reaction system having a positive temperature coefficient. If any variable is changed so that the reaction rate slowly rises, the temperature tends to rise above the surroundings. As soon as the temperature rise necessary to dissipate the heat has an appreciable effect on the reaction rate, the variable being subjected to slow change may lose control. This loss of control is the common feature of all ignition-point determinations. Differences arise in the conditions under which the loss of control occurs and in the criteria for its determination.

Using selected samples of 60- to 90-mesh vitrain, clarain, and durain, Newall and Sinnatt [32] determined the number of particles that ignited when dropped through a heated tube. They found that temperatures of the order of 700° C (1,292° F) were necessary to ignite a major fraction of the coal particles, although some particles ignited as low as 600° C (1,112° F). In a more recent investigation,[33] using low-density fractions of certain bituminous coals, it was found that temperatures in excess of 800° C (1,472° F) were necessary to obtain uniform ignition of 60- to 80-mesh particles.

These furnace temperatures, needed to bring about ignition of individual falling particles, should not be compared with ignition temperatures as determined in beds of broken coal. Owing either to the ease of elimination of the heat of combustion, to the short time of heating, or to changes in the particle, ignition may fail at temperatures far above those required for ignition in the bed.

Up to a certain point in the temperature history of a particle, the temperature of the surroundings could be reduced and the particle temperature would promptly follow. Beyond this point, the particle temperature would continue to rise but its subsequent history might depend upon the rate of heating and the temperature at the time of removal of the external heat source. Photographic records of burning coal particles have shown brilliant initial traces attributed to the combustion of volatile matter.[33, 34] These traces generally occurred at furnace temperatures above 900° C (1,652° F). Otherwise they were frequently absent even though the remaining

32 Newall, H. E., and Sinnatt, F. S., *Fuel*, **5**, 335 9 (1926).

33 Orning, A. A., *Trans. Am. Soc. Mech. Engrs.*, **64**, 497–506 (1942).

34 Griffin, H. K., Adams, J. R., and Smith, D. F., *Ind. Eng. Chem.*, **22**, 808–15 (1929).

trace, attributed to the burning coke residue, was present.

The problem is further complicated by the unknown sequence of the effects of heat on the coal particle. Whether oxidation begins to contribute to the temperature rise before or after the loss of volatile matter is not known. It is possible for ignition to occur either in the gas phase or on the solid surface. With occasional particles igniting at low furnace temperatures, it probably occurs at the surface. At higher temperatures, ignition may still occur at the surface followed by flame propagation into escaping volatile matter, but direct ignition of the volatile matter cannot be excluded.

Assuming that the particle on entering the furnace receives energy by radiation and loses energy by conduction to surrounding gases, Nusselt has calculated ignition times.[35] An assumption of infinite excess air led to the anomalous result [36] that ignition might fail owing to a dependence of the maximum temperature upon the particle diameter. The following formulas are derived from Traustel's extension to finite excess air supply: [37]

$$\frac{1}{D} = \frac{1 - e^{-n}}{2\left(1 + \frac{1}{N}\right)^2} + \frac{2Z}{(N+1)D^2} \quad (1)$$

$$D = \sigma T_r^4 \frac{d}{kT} \quad (2)$$

$$Z = 3\sigma^2 T_r^8 \frac{t}{ckT^2} \quad (3)$$

$$n = 4\left(1 + \frac{1}{N}\right)\frac{Z}{D^2} \quad (4)$$

35 Nusselt, W., Z. Ver. deut. Ing., 68, 124–8 (1924).
36 Mayers, M. A., Trans. Am. Inst. Mining Met. Engrs., 119, 304–20 (1936).
37 Traustel, S., Feuerungstech., 29, 1–6, 25–31, 49–60 (1941).

$$n = 4\left(1 + \frac{1}{N}\right)\frac{3kt}{cd^2} \quad (5)$$

The dimensionless quantity N is the ratio of the heat capacities of the associated quantities of air and coal and hence is a measure of the excess air. The remaining notation, except for the dimensionless quantities, D, Z, and n, are: t = time; d = particle diameter; T = particle temperature; T_r = effective radiation temperature; σ = Stefan-Boltzmann constant; k = thermal conductivity of air; and c = heat capacity per degree per unit volume of particle. Both the particle and the air are assumed to be at zero temperature at zero time. Heat loss by radiation from the particle is neglected.

For small values of n the exponential may be replaced by the first two terms of its expansion and:

$$D = 2Z \quad (6)$$

or

$$T = \frac{6\sigma T_r^4}{cd} t \quad (7)$$

For large values of n the exponential may be neglected (95 percent accuracy or better for n greater than 3).

$$\frac{1}{D} = \frac{1}{2\left(1 + \frac{1}{N}\right)^2} + \frac{2Z}{(N+1)D^2} \quad (8)$$

or

$$T = \sigma T_r^4 \left\{ \frac{N^2 d}{2(N+1)^2 k} + \frac{6t}{(N+1)cd} \right\} \quad (9)$$

The particle temperature is directly proportional to the intensity of radiation. The rate of rise of temperature is inversely proportional to the diameter and is initially rapid and independent of excess air. The period of rapid rise ends (n becomes larger than some arbitrary value) at a time proportional to the square of the diameter and at a temperature which is proportional to

the diameter and which is also insensitive to high excess air. The final constant rate of rise is less than the initial in proportion to the ratio of the heat capacity of the coal to the heat capacity of the coal plus the air in which it is suspended.

Although unknown ignition temperatures and heating due to slow oxidation make calculated ignition times highly uncertain, it is possible to estimate the influence of various factors. With highly reactive coals, the ignition temperature may fall within the region of rapidly rising temperature. With such coals there is no necessity for limiting the amount of primary air. The finest particles will generally be the first to ignite. It can be shown that, with N greater than 4.58, there is an intermediate size range within which the time required to reach a given temperature decreases with increasing particle size. With highly reactive coals and unlimited primary air, the early ignition of intermediate-sized particles may aid flame stability. Less reactive coals require finer pulverization and limited primary air. Since the factor $N + 1$ cannot approach zero, the effect of reducing primary air is limited. The finest particles will always be the first to ignite.

FLAME PROPAGATION

Almost any combustible dust, when suspended in the proper proportion of air, is more or less explosive. Various government agencies, with special regard to industrial hazards and safety in mines, have made extensive investigations of the conditions under which such explosions can occur. Several publications of the U. S. Bureau of Mines review this work and include extensive bibliographies.[38] The important

conclusion has been that such explosions can be prevented by the addition of inert rock dust. The amount of inert matter required increases regularly with the ratio of volatile to total combustible matter. There appears to be some correlation between this result and the ease of igniting and burning various coals in the pulverized-coal furnace.

The measurements of flame velocities are not applicable to furnace conditions. Such explosions involve a flame front moving into surroundings at low temperatures and occur in air which, after the start of the explosion, is at pressures considerably above 1 atmosphere. They also undergo acceleration, further complicating any application to stationary flames.

In connection with the French work on safety in mines, a series of experiments was carried out in which coal-dust flames were produced in a conical tube. These experiments were made to determine the rate of flame propagation as a function of the coal composition and the amount of excess air. Supposedly on the basis of this work, De-Grey [39] prepared a set of curves showing the flame velocity as a function of the coal-to-air ratio and the proximate analysis of the coal. These curves have been reproduced, at times with transformed coordinates, at a number of places in the literature. There is no reason to believe that they are not qualitatively correct. On the other hand, the published reports of the original experimental work [40] do not alone justify the quantitative values implied by

Tech. Paper **464** (1929), 45 pp. Hartmann, I., Howarth, H. C., and Greenwald, H. P., *ibid.*, **617** (1940), 45 pp.

39 DeGrey, A., *Rev. mét.*, **19**, 645–55 (1922).

40 Taffanel, J., and Durr, A., *Cinquième série d'essais sur les inflammations de poussières, essais d'inflammabilité,* Comité central des houillères de France, Paris, 1911, 70 pp. Taffanel, J., *Ann. mines*, (11), **2**, 167–205 (1912). Taffanel, J., and Durr, A., *Colliery Guardian*, **103**, 227–8 (1912).

38 Rice, G. S., *U. S. Bur. Mines, Bull.* **20** (1911), 204 pp. Rice, G. S., Jones, L. M., Egg, W. L., and Greenwald, H. P., *ibid.*, **167** (1922), 639 pp. Greenwald, H. P., *U. S. Bur. Mines,*

the family of curves. Only one coal was cited, and considerable doubt was expressed as to the accuracy of the results. The values given for the different coals seem to be qualitatively based on the ease of preventing dust explosions with rock dust. No other justification has been found except possibly the measured rates of propagation of explosion waves. However, these waves showed continual acceleration and can only imply relative differences in stationary flames.

In a given installation it will generally be found that, at some velocity of coal and air flow, the flame tends to blow away from the burner mouth. The files of operating companies and equipment manufacturers probably contain considerable information on such blow-off velocities. No survey or correlation of such data has been found.

Even though adequate information on flame velocities were available, it might prove difficult to interpret blow-off velocities. The gas velocity and cloud density at the burner mouth are rarely, if ever, uniform. This nonuniformity may actually be necessary to flame attachment. Where the stream of primary air and coal is given a whirling motion in the burner tube, centrifugal action concentrates the coal in the periphery of the stream where drag on the tube wall produces a minimum gas velocity. Such a region would appear to be a likely place for attachment of the edge of the flame front. Once attachment is obtained the proximity of burning particles and the possibility of a continuous gas-phase flame front in escaping volatile matter [32, 33] favor the propagation of the flame front into regions of high velocity and low cloud density.

Flame attachment and propagation depend upon the primary ignition of a few particles. It might be supposed that they would be the finest particles in the cloud,

but no direct experimental evidence is available for their identification. Increasing fineness of pulverization increases the heat release in the neighborhood of the flame front, thus favoring rapid ignition without necessarily inferring easier ignition of the fine particles.

THE BURNING PARTICLE

In order to calculate burning times, it has generally been assumed that the burning particle was a homogeneous solid. Pores and ash inclusions were admitted, but the dimensions of such irregularities were assumed small as compared to the particle size. If not specifically stated, this was a necessary consequence of the assumption that the rate of change of diameter was a measure of the rate of burning and that zero diameter determined the end of the combustion period.

This assumption was probably correct for particles like anthracite or fusain. For particles of caking coals it is subject to considerable doubt. When such particles are dropped through an inert atmosphere in a heated tube, they form hollow shells or cenospheres.[32, 41] Since the presence of cenospheres in flue dust is indicative of incomplete combustion, it is natural to suppose that they are produced only when conditions are unfavorable. However, incomplete combustion is essential to the available evidence on the configuration of the burning particle. With flame temperatures above the ash-fusion temperature, an ash residue could not be expected to retain the configuration of the particle from which it came.

When individual particles of caking coals

41 Sinnatt, F. S., and Slater, L., *Fuel*, **1**, 2–3 (1922). Newall, H E., and Sinnatt, F. S., *ibid*, **3**, 424–34 (1924). Sinnatt, F. S., *Proc. 2nd Intern. Conf. Bituminous Coal*, **1**, 560–85 (1928) ; *J. Soc. Chem. Ind.*, **47**, 151-5T (1928) ; *Fuel*, **8**, 362–70 (1929).

are dropped through a furnace in an oxidizing atmosphere,[32, 33] the residues either are cenospheres or, with the finer sizes, escape collection in the equipment. The form of the residues depends upon the furnace temperature,[33] varying from slightly rounded edges to well-formed cenospheres. These cenospheres are more irregular than those obtained in an inert atmosphere. Some have hollow nodules apparently formed by the escape of plastic material through a weak spot in an initial surface.

The cenosphere size first increases and then passes through a maximum at about the temperature required to cause uniform ignition. Above the igniting temperature up to the highest furnace temperature, 950° C (1,742° F), the size decreases. This indicates that the initial size of the burning cenosphere is less than those obtained at lower temperatures. The residues, although highly etched and pitted by combustion, are still cenospheres with no evidence that they have been formed, by reduction in diameter, from a larger coke structure.

The mechanism of formation of cenospheres is not well understood. With those particles that melt on rapid heating, the simultaneous evolution of volatile matter tends to blow them into a froth. It appears that distillation and oxidation increase the viscosity of the surface while the interior is still highly plastic. Under these conditions the bubbles coalesce, forming one big bubble or cenosphere. The rate of gas evolution and the rate of hardening govern the size. These factors are influenced both by the characteristics of the coal and by the temperature of the furnace, which in turn may depend upon the geometry of the furnace. The controlling factor is probably the rate of rise of surface temperature, but this rate is not readily determined.

The formation of cenospheres depends upon simultaneous softening and evolution of volatile matter. Anthracites do not soften. Some coals conceivably might not soften enough to destroy a cokelike bubble structure. No evidence for such structures has been found. Others might lose volatile without softening, leaving a char that has the configuration of the original particle.

MECHANISM OF COMBUSTION

The combustion of coal defies anything more than a superficial description. It may be divided roughly into gasification of the solid and burning of any combustible gases. The exact nature of the reactions is of immediate importance only with regard to rates of burning.

The standard procedure of proximate analysis specifies the sample, the crucible, and furnace conditions. There is no assurance that the amount of volatile matter determined under these conditions corresponds to that burning as a gas in the pulverized-coal flame. Aside from differences in pyrolysis, gasification of the solid residue probably produces carbon monoxide.

Photographic studies have indicated the presence of a luminous gas flame under certain conditions.[34, 34] Further amounts may have burned in a nonluminous flame. Volatile matter that is forcibly ejected will burn rapidly in the surrounding air. If it is evolved slowly it may burn so close to the surface as to be indistinguishable from combustion of the solid residue.

The chemical character of the residue is unknown. Partial combustion transforms the appearance of cenospheres from that of hard pitch to graphite.[33] Chemical properties probably undergo just as great a change. Lack of data on the combustion of carbonaceous solids makes it necessary to rely on the information available for carbon.

Experimental work on the chemistry of the combustion of carbon has been adequately reviewed.[42] Apparent contradictions between the results of different experimental techniques are indicative of a failure to consider all the variables. When it was found necessary to provide a uniform coat of oriented graphite crystals before reproducible results could be obtained with a filament in oxygen at low pressure,[43] it could hardly be expected that the results would correlate with all the various forms and states of aggregation of carbon. Oxygen that cannot be removed from carbon by evacuation as such can be removed by evacuation and heating as mixed oxides. Such oxygen is probably held by primary valence forces. Although there are comparatively few ways that oxygen can bond with carbon, there is an infinite variety of locations with respect to the gross crystal. The different reaction rates, temperature coefficients, and dependences on gas pressure that are found in different temperature regions and at atmospheric and low pressures probably result from the different molecular types that are stable or that can contribute to the reaction mechanism at the different temperatures and pressures.

Applying the information on carbon to the burning solid residue, oxygen, carbon dioxide, and water must be considered as oxidants. These gases are adsorbed on the surface, a rearrangement of bonds occurs, and combustion products are eliminated. Reaction with oxygen produces a mixture of carbon monoxide and dioxide. A secondary reaction with carbon dioxide produces additional monoxide. Reaction with water produces carbon monoxide, hydrogen, and possibly methane. Evidence for the direct formation of carbon dioxide is obscured by the water-gas reaction. The rates of the various reactions depend upon the temperature and partial pressures at the solid surface. Although zero-order reaction rates have been found at low pressures, the rates are much higher at atmospheric pressures and, for electrode carbon burning in an air stream, a first-order dependence upon the partial pressure of oxygen has been found.[44]

Assuming that carbon dioxide was the only oxidant, oxygen being consumed by the resulting carbon monoxide before reaching the surface, the rate of burning of small carbon spheres has been calculated.[45] The analysis was reasonably sound except for the failure to locate the boundary between the carbon monoxide and oxygen layers. Actually there must have been a region in which both gases were present. If this region extended to the carbon surface, the basic assumption was not tenable.

Using a microsampling technique, Parker and Hottel determined the gas composition at a carbon surface burning in an air stream.[44] Above about 700° C (1,292° F) surface temperature, the oxygen concentration decreased rapidly, and above 1,200° C (2,192° F) asymptotically approached zero. Small concentrations of carbon monoxide were found. An assumption that appreciable amounts were present but had burned to carbon dioxide in the sampling tube would have indicated even higher oxygen concentrations. The results might have been different had the approaching gas stream contained high carbon dioxide and depleted oxygen concentrations.

42 Mayers, M. A., *Chem. Revs.*, **14,** 31–53 (1934). Strickland-Constable, R. F., *Fuel,* **19,** 89–93 (1940). Bangham, D. H., and Bennett, J. G., *ibid.,* **19,** 95–101 (1940).

43 Meyer, L., *Z. physik. Chem.,* **B17,** 385–404 (1932).

44 Parker, A. S., and Hottel, H. C., *Ind. Eng. Chem.,* **28,** 1334–41 (1936).

45 Burke, S. P., and Schumann, T. E. W., *Proc. 3rd Intern. Conf. Bituminous Coal,* **2,** 485–509 (1931).

Tu, Davis, and Hottel [46] measured the rate of loss of weight of 1-inch spheres of electrode carbon burning in an air stream within an electric furnace. The rate was proportional to the partial pressure of oxygen in the approaching gas stream. Up to about 800° C (1,472° F) it was independent of air velocity and increased rapidly with increasing temperature. At higher temperatures the rate increased with about the 0.4 power of the air velocity and with the 0.6 to the 1.1 power of the absolute temperature. Similar measurements were made by Smith and Gudmundsen [47] except that 5-millimeter spheres were allowed to burn to 1 millimeter. Mayers' analysis of their results [48] showed the rate to be proportional to the diameter and to the 0.4 power of the air velocity, but no consistent relation was found between the rate and furnace temperature.

These results clearly indicated that the rate of transport of oxidant to the surface, rather than the surface reaction, became the controlling factor at high temperatures. Davis and Hottel [49] attempted to isolate the transport factor by measuring the rate of burning of carbon disks set in the bottom of cups of different depths. Their results were not conclusive. Samples of wood charcoal and of brush carbon gave different results. A dependence of the proportion of carbon monoxide, produced in the primary reaction, upon the nature of the carbonaceous material was proposed as a possible explanation.

A microsampling technique has been used to determine gas compositions within the diffusion film near a burning carbon surface.[44] The concentration gradients were not determined close enough to the surface to eliminate the effect of carbon dioxide originating at considerable distances from the plane of sampling. The application to the determination of diffusion coefficients must be judged accordingly. The results were indicative of the structure of convection-diffusion systems but were not extensive enough for complete analysis.

The rate of flow of oxygen in a convection-diffusion system is proportional to the product of the partial pressure by the velocity, minus the diffusion constant times the gradient of the partial pressure. Mayers [48] has imposed the condition that the divergence of the flow must be zero except at a source or sink of oxygen but was unable to solve the resulting differential equation. No solutions have been found for any of the cases of interest in which the gas velocity becomes zero at a bounding surface. All theoretical calculations of burning rates have involved simplifying assumptions to avoid solution of this general problem.

Nusselt [35] neglected the gas velocity and assumed that the burning coal particle was a sphere burning at such a high rate that the partial pressure of oxygen was reduced to zero at the surface. For infinite excess air supply the rate of burning was found to be proportional to the radius and to the partial pressure of oxygen at infinity. The condition of infinite excess air was removed by assuming that the pressure at infinity could be replaced by the mean gas pressure. Considering that the total volume was large, compared to that of the particle plus the surrounding region of appreciably reduced pressure, this was a reasonable assumption.

Various investigators [44, 45, 46, 50] have in-

46 Tu, C. M., Davis, H., and Hottel, H. C., *Ind. Eng. Chem.*, **26**, 749–57 (1934).

47 Smith, D. F., and Gudmundsen, A., *ibid.*, **23**, 277–85 (1931).

48 Mayers, M. A., ref. 42.

49 Davis, H., and Hottel, H. C., *Ind. Eng. Chem.*, **26**, 889–92 (1934).

50 Burke, S. P., and Schumann, T. E. W., *ibid.*, **23**, 406–13 (1931), **24**, 451–3 (1932).

troduced the influence of relative velocity between the gas and the particle by making the assumption, similar to that made in the study of heat transfer, that turbulent flow wiped out all concentration gradients except for a stagnant diffusion layer adjacent to the surface. This device has permitted empirical correlations of the data on rates of burning of large spheres but contributes a negligible factor for the low relative velocities that probably exist in the pulverized-coal furnace.[44]

The dependence of diffusion constants upon temperature inseparably connects the calculation of burning rates with the estimation of particle temperature. The heat and mass flow equations may be written in the form:

$$H = -k \left(\frac{T}{273} \right)^n \text{grad } T \qquad (10)$$

and

$$M = -D \left(\frac{T}{273} \right)^{n+1} (RT)^{-1} \text{grad } p \qquad (11)$$

The difference of 1 power in the temperature coefficients, although approximately correct, is arbitrarily chosen to permit easy integration in any region where the gradient vectors are parallel.

$$\frac{T_2 - T_1}{p_2 - p_1} = \frac{H}{M} \frac{D}{k} \frac{1}{273R} \qquad (12)$$

Using the approximate values,

$$D = 0.178 \text{ cm}^2/\text{sec} \qquad (13)$$

and

$$k = 5.33 \times 10^{-5} \text{ cal/cm/sec/°C} \qquad (14)$$

$$\frac{T_2 - T_1}{p_2 - p_1} = 0.149 \frac{H}{M} \qquad (15)$$

Assuming no loss by radiation and a partial-pressure drop from that of oxygen in air to zero, the temperature rise would be of the order of 3,000° C (5,432° F). Such enormous temperature differences do not occur. The temperature of a burning particle will rise sufficiently above the effective

radiation temperature of its surroundings to lose part of the heat by radiation.

The temperature history of a typical particle of 60- to 80-mesh Pittsburgh Seam coal burning in a furnace at 950° C has been estimated,[33] Fig. 21. There was considerable uncertainty in the temperatures, but the general features of the curve were
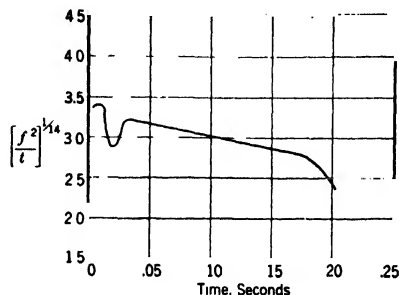
undoubtedly correct. The first maximum, about 1,800° C (3,272° F), was attributed to the combustion of volatile matter. The minimum, about 1,500° C (2,732° F), resulted from local depletion of oxygen due to the gas-phase combustion. Diffusion of oxygen to the surface brought about the second maximum. The period of slowly falling temperature corresponded to combustion limited only by the rate of diffusion. The final rapid fall indicated quenching action due to the high temperature coefficient of the surface reaction beginning to limit the rate at about 1,400° C (2,552° F). Although the residues still contained about 70 percent combustible, rapid combustion ceased at temperatures considerably above those found for electrode carbon.[44, 46] High temperatures and ash accumulations must have reduced the reactivity.

At high temperatures it appears certain that the rate of burning will depend only upon the rate of transport of oxidant to the surface. Any gasification by carbon dioxide or water will probably increase the rate.[37] These reactions appear to be too slow [46, 51] to account for the measured burning rates. However, it is possible that they may be more rapid in the presence of a simultaneous reaction with oxygen.

At lower temperatures, the rate of the surface reaction begins to control. This generally happens somewhere between 1,400 and 1,000° C (2,552 and 1,832° F), depending upon the reactivity of the burning particle. It has been assumed that the "chemical resistance" of burning coal particles would be less than that of electrode carbon.[52] This may be true for the original coal, but the high temperatures in the early part of the burning process probably reduce the reactivity to a value more nearly comparable to that of graphite.

THEORETICAL BURNING TIMES

Various investigators [35, 37, 44, 45, 46, 50] have used the available information on diffusion constants and the mechanism and rate of combustion of carbon spheres to calculate burning times. Assuming a sphere burning in an infinite amount of stagnant air, the partial pressure of oxygen is given by:

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(\frac{Dr^2}{RT}\frac{\partial p}{\partial r}\right) = 0 \qquad (16)$$

Avoiding obvious difficulties by assuming isothermal conditions:

$$p = p_s + (p_\infty - p_s)\left(1 - \frac{r_s}{r}\right) \qquad (17)$$

The number of moles of oxygen reaching the sphere in unit time is

[51] Mayers, M. A., *J. Am. Chem. Soc.*, **56**, 70–6, 1879–81 (1934), **61**, 2053–8 (1939).
[52] Hottel, H. C., and Stewart, I. McC., *Ind. Eng. Chem.*, **32**, 719–30 (1940).

$$K = 4\pi r_s^2 \frac{D}{RT}\frac{\partial p}{\partial r}\bigg|_{r=r_s} \qquad (18)$$

or

$$K = \frac{4\pi D}{RT}(p_\infty - p_s)r_s \qquad (19)$$

In order to avoid the assumption of isothermal conditions, equation 16 should have been solved simultaneously with a similar equation governing the flow of heat. However, the solution appears to be rather insensitive to the temperature corrections.[35, 37, 45, 50] In view of the uncertainty in the dependence of diffusion constants upon temperature it appears better to take the isothermal solution and to indicate that the result should be approximately correct provided that some sort of a mean gas temperature is used.

Assuming the burning sphere to be a homogeneous solid:

$$-4\pi a^3 \rho^2 \frac{\partial \rho}{\partial t} = KL \qquad (20)$$

where ρ is the fraction of the initial radius a, and L is the volume of solid equivalent to one mole of oxygen. Introducing equation 19, the time required to burn to the fractional radius ρ_1 is

$$\theta = \frac{a^2 RT}{DL}\int_{\rho_1}^{1}\frac{\rho d\rho}{p_\infty - p_s} \qquad (21)$$

The condition of infinite excess air may be removed by replacing the pressure at infinity with the mean partial pressure of oxygen. Assuming an amount of excess air e, when ρ equals ρ_1,

$$p_m = \frac{0.21}{1+e}\left(e + \frac{\rho^3 - \rho_1^3}{1 - \rho_1^3}\right) \qquad (22)$$

This correction is too severe. It places the mean partial pressure at infinity, whereas in a uniform suspension it would be closer to the particle than half the distance to its nearest neighbor. A better approximation would be obtained by solving the time-dependent diffusion equation in a region confined by a concentric sphere just large

enough to contain the given amount of excess air. However, this equation apparently does not lead to a closed solution.

Replacing the pressure at infinity in equation 21 by the mean pressure from equation 22,

$$\theta = \frac{a^2 RT}{0.21 DL} (1 + e)(1 - \rho_1{}^3)$$
$$\int_{\rho_1}^1 \frac{\rho d\rho}{k_1{}^3 + \rho^3} \quad (23)$$

$$k_1{}^3 = (1 - \rho_1{}^3)e - \rho_1{}^3 -$$
$$(1 + e)(1 - \rho_1{}^3) \frac{p_e}{0.21} \quad (24)$$

Equation 23 contains the partial pressure of oxygen at the burning surface. Assuming it to be zero gives the minimum burning time but, for high furnace temperatures, probably does not introduce a serious error.

$$\theta = \frac{a^2 RT}{0.21 DL} f(e, \rho_1) \quad (25)$$

$$f(e, \rho_1) = \frac{(1 + e)(1 - \rho_1{}^3)}{3k} \left\{ \frac{3}{2} \log \frac{k^2 - k + 1}{k^2 - k\rho_1 + \rho_1{}^2} = \right.$$
$$\left. -\log \frac{1 + e}{e} + \sqrt{3} \tan^{-1} \frac{2 - k}{k\sqrt{3}} - \sqrt{3} \tan^{-1} \frac{2\rho_1 - k}{k\sqrt{3}} \right\} \quad (26)$$

where $\quad k^3 = (1 - \rho_1{}^3)e - \rho_1{}^3 \quad (27)$

If ρ_1 had been set equal to zero, equation 26 would have been identical with the dependence of burning time upon excess air as given by Parker and Hottel.[44] However, for coals that form cenospheres, with their mass assumed to be concentrated between two concentric spheres, the particle cannot burn to zero radius. Letting a_0 be the radius of a solid sphere equivalent to a cenosphere of radius a and fractional radius to the inner surface ρ_1, equation 26 becomes

$$f \left(e, \frac{a_0}{a} \right) = \frac{1 + e}{3k} \left(\frac{a_0}{a} \right)^3 \left\{ \frac{3}{2} \log \frac{k^2 - k + 1}{k^2 - k\rho_1 + \rho_1{}^2} - \log \frac{1 + e}{e} + \sqrt{3} \tan^{-1} \frac{2 - k}{k\sqrt{3}} \right.$$
$$\left. - \sqrt{3} \tan^{-1} \frac{2\rho_1 - k}{k \sqrt{3}} \right\} \quad (28)$$

since

$$a_0{}^3 = a^3(1 - \rho_1{}^3) \quad (29)$$

Since equations 27 and 29 may be used to eliminate ρ_1 and k, equation 28 indicates that the burning time of a cenosphere is proportional to the square of the radius of an equivalent solid sphere and to a function depending only upon the excess air and the expansion ratio, which is the ratio of the diameter of the cenosphere to that of the equivalent solid sphere. The last function is plotted against the inverse ratio for various excess-air values in Fig. 22. For high expansions the curves are nearly linear. The dotted lines are given by

$$\frac{a^2}{a_0{}^2} f \left(e, \frac{a_0}{a} \right) = \frac{1 + e}{3} \frac{a_0}{a} \log \frac{1 + e}{e} \quad (30)$$

For small expansions the curves rise above the straight lines and approach infinite slope as the ratio approaches 1.

Anthracites are generally more difficult to burn than bituminous coals.[24] There is probably some difference in reactivity. However, the reactivity of the original coal is no indication of the reactivity of the burning residue, and, except in ignition and the completion of burning, reactivity probably is not a controlling factor. The increasing portion of the mass that must burn in a heterogeneous surface reaction might indicate a continuous increase in burning time with decreasing volatile content. Such a variation probably exists but does not appear to be enough to explain the difference between anthracite and low-volatile bituminous coals. The sharp drop in calculated times for cenospheres as compared to the equivalent solid spheres sug-

gests that the bituminous coals generally form cenospheres while the anthracites must be considered homogeneous solids.

Considerable care must be taken in any attempt to correlate the calculated burning times with actual furnace conditions. No neglect this time. The error is compensated by an excessive correction for finite air supply.

The calculated burning times have been based on diffusion as the controlling factor. In cold furnaces there may be a residue
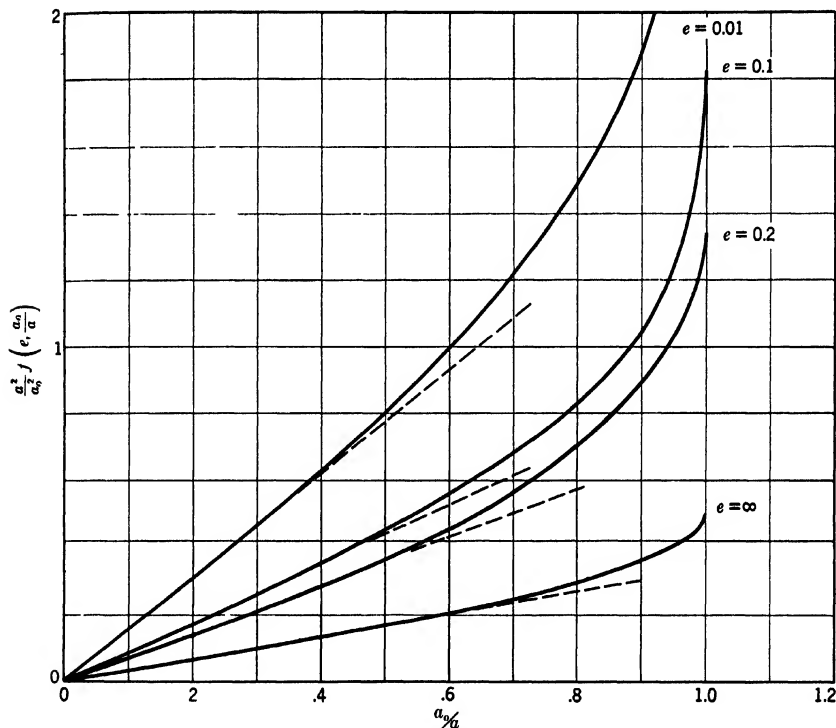
FIG. 22. Dependence of burning time upon cenosphere expansion and excess air. (e = excess air, a = radius of cenosphere, a_o = radius of a solid sphere of equal weight.)

allowance has been made for the combustion of volatile matter. In the absence of any basis for calculation it has usually been assumed either that the volatile matter burns simultaneously with the fixed carbon or that its burning time is negligible. Since the photographic studies have indicated a short brilliant flame attributed to combustion of volatile matter,[33, 34] it is best to subject to continued combustion at a slower rate because of the high temperature coefficient of the surface reaction. This corresponds to a finite partial pressure of oxygen at the burning surface. If this pressure is nearly equal to the mean partial pressure of oxygen in the surroundings, the rate of burning will be so low that the added combustion will be negligible. In

the intermediate range the partial pressure must be such that the amount of oxygen reaching the surface, equation 19, is just equal to its rate of consumption, that is,

$$\frac{K}{4\pi r_s{}^2} = \frac{\alpha p_s}{\sqrt{T_s}}\, e^{-E/RT_s} \qquad (31)$$

Using appropriate values for the constants,[44] equation 31 may be solved with equation 19 and the resulting values for p_s used in the graphical integration of equation 23. This procedure requires accurate information on particle temperatures not at present available.

Experimental Burning Times

The only available data comparable to actual furnace conditions on burning times of sized coal are those given by Audibert.[53] Two closely sized samples of various coals were burnt with different amounts of excess air in a vertical refractory tube. The point of complete burning was determined from gas analyses. The burning time was determined from the rate of air flow, allowance being made for thermal expansion and an estimated relative velocity between particles and gas. Except for a lignite and the coarser size of one high-volatile coal, the burning time was found to increase with increasing volatile content, a result directly opposed to the observation of American coals in industrial furnaces.[30]

Audibert's data cannot be readily interpreted. A typical set of data, presented as smooth curves without experimental points, indicated that the end point could be determined with reasonable accuracy, although continued slow combustion could not be detected. The tube was preheated by burning charcoal in the bottom. Otherwise it was heated only by the pulverized-coal flame. The wall temperature, reported for only one experiment, fell below 1,400° C (2,552° F) within the combustion zone. Under such conditions the rate of the surface reaction was probably the controlling factor at the end of the combustion period. It is possible that incomplete combustion may have been responsible for the peculiar variation of burning time with volatile content. Lack of data on the combustible contents of the ash residues makes it impossible to test this hypothesis.

Rosin[54] has given the formula

$$Z = \frac{1,000}{(F/G)^{1.8}} \qquad (32)$$

for the burning time in seconds as a function of the particle surface in square millimeters F, and the weight in milligrams G. This formula was applied to a German brown coal in a furnace at 1,300° C (2,372° F). It appears to have been based on industrial experience, but no original data have been located. It gives burning times that are somewhat larger and increase more rapidly with particle size than Audibert's findings indicated.

The environment of an individual particle in a flame is neither constant nor readily determined. Although photographic investigations have failed to simulate actual flame conditions, they have made it possible to isolate the effect of a known environment on the combustion of a single particle. The method involves photographs, taken on a moving film, of particles fed at a slow rate into an electric furnace. With particle and film motions at right angles to each other, the component, along the direction of film motion, of the distance from the beginning to the end of the trace becomes a measure of the time during which the particle was sufficiently incandescent to register on the film.

[53] Audibert, E., *Rev. ind. minérale*, **4**, 1–32 (1924).

[54] Rosin, P., *Braunkohle*, **24**, 241–59 (1925).

Griffin, Adams, and Smith[34] photographed burning particles of a coal, a semi-coke, a beehive coke, and an active charcoal. At 1,000° C (1,832° F), rarely at 750° C (1,382° F), the coal showed brilliant initial traces which were occasionally found with the cokes but not with the charcoal. The brilliant trace was supposed to be due to the combustion of volatile matter; the remaining trace corresponded to the burning solid residue. Since a recording paper and a panchromatic film having different speeds and spectral sensitivities gave nearly the same result, it was assumed that the time of photographic incandescence was the burning time. Several explanations were proposed for the unexpected result that the burning time increased with rising furnace temperature. The possibility of incomplete combustion was rejected without any specific evidence.

The unknown effective exposure times for the continuous traces make it difficult to compare the different investigations. Godbert[55] concluded that his photographs corresponded to the initial brilliant traces obtained by Griffin, Adams, and Smith.[34] His data should be interpreted as applying to the burning time of the volatile matter. The time was inversely proportional to the specific surface and decreased with increasing reactivity (measured by the rate of oxygen absorption). It varied from about 2 to 8 milliseconds in the range from 80- to 200-mesh (I.M.M.). Since this was a small part of the total burning time, the other investigations were not suited to its determination but they were in qualitative agreement.

The earlier investigations lacked sufficient data either to establish the degree of

55 Godbert, A. L., *Fuel*, **9**, 57–75 (1930). Godbert, A. L., and Wheeler, R. V., *Safety in Mines Research Board (London), Paper* **73** (1932), 21 pp.

combustion or to determine the relation between burning and photographic incandescence. A later investigation[33] showed by analysis and microscopic examination of residues that temperatures above 800° C (1,472° F) were needed for uniform ignition and that combustion was not complete even at 950° C (1,742° F) furnace temperature. It was also found that Eastman Super-XX Panchromatic roll film with an f:3.7 lens was able to record the incandescence into the region of rapidly falling temperature attributed to the controlling effect of the surface reaction. Since the rate of burning in this region was probably too slow to add appreciably to the degree of combustion, the burning time was defined as the period from the point of ignition to the onset of the final rapid fall in temperature.

On the basis of these results it appeared probable that Griffin, Adams, and Smith were approximating the burning time and that their negative temperature coefficients resulted from a dependence of the degree of combustion upon furnace temperature. It is possible, however, that a variation of cenosphere size with furnace temperature[33] may have affected the burning rate. The comparatively small temperature coefficient for active charcoal makes this seem plausible.

The available data on the photographic burning times for coal at 950° C (1,742° F) are shown in Fig. 23. These are burning times at constant furnace temperature and not at constant degree of combustion. They do not include the period of slow combustion during which the particle is no longer able to maintain a temperature substantially above its surroundings. These limitations may not be serious. For particles finer than 80-mesh, combustion was probably better than 90 percent complete.[33] The burning time varies approxi-

mately as the square of the diameter. This is further evidence that the photographic burning time actually corresponds to the theoretical time calculated on the basis of diffusion as the controlling factor.

Hottel and Stewart [52] concluded that the specific combustion rate (the rate per unit surface area) should be expressed by the formula

$$k = A \frac{p}{d^m} \qquad (33)$$

where A is a constant depending upon temperature, p is the partial pressure of oxy-
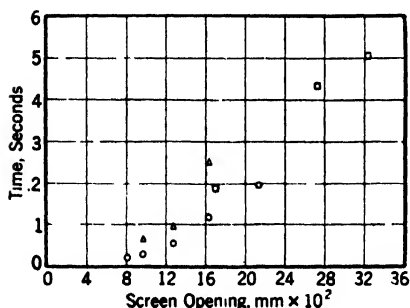
FIG. 23. Burning time as function of mean screen opening.[53] (○ 1.29 = float Pittsburgh Seam coal; △ 1.35 = float Pocahontas Seam coal, □ = Kanawha gas coal.)

gen, and d is the particle diameter. On the basis of this formula and the Rosin-Rammler law of size distribution,[56] they calculated the unburnt carbon as a function of time for a pulverized-coal flame. Comparing their results with Sherman's experimental data [50] they found that $m = 0$ gave a better correlation than $m = 0.5$ and indicated that even better results might be obtained by setting m equal to -0.4.

Since setting m equal to zero in equation 33 is equivalent to a burning rate proportional to the particle surface, it would ap-

56 Rosin, P., and Rammler, E., J. Inst. Fuel, 7, 29–36 (1983).

pear that the surface reaction rate was the controlling factor in Sherman's experiments. However, the initial dust sampling point was generally near the point of maximum temperature, and the unburnt carbon at this point was less than 25 percent except for Pocahontas coal, ranging to a maximum of 50 percent in a relatively cold furnace. The calculated rate of heat release per unit volume [52] was highly peaked in the early stages. It was estimated that just as long a time was required to burn from 2.0 to 0.35 percent as to burn freshly ignited fuel to a residue of 2.0 percent unburnt carbon. This indicates that the correlation was mainly dependent upon the rate of burning of the coarser particles in that part of the furnace where the temperature was such that the surface reaction was beginning to control.

Considering all the data on the mechanism and rate of combustion, it appears that a transition must occur from diffusion to surface reactivity as the controlling factor. Immediately after the zone of ignition and burning of volatile matter, the particle temperature rises very rapidly. In this region the smaller particles burn to a low carbon content within a time proportional to the square of the radius of an equivalent solid sphere and to a function depending upon the influence of coal characteristics and flame conditions upon cenosphere formation.

The larger particles will still contain a considerable portion of the total carbon after the rate of heat release has passed its peak. Continued rapid combustion of these particles depends upon their ability to maintain themselves above a certain temperature. With the combustion rate, and hence the heat release, varying as the particle diameter while the rate of loss by radiation is proportional to the surface, the

largest particles will have the lowest temperature.

The reactivity of the original fuel is no indication of the temperature at which the surface reaction begins to control. The high particle temperatures in the early stages of combustion transform the residue into a material whose reactivity is mainly a function of flame conditions. The characteristics of the original fuel appear in their effect on cenosphere formation, in a possible catalysis by ash, and in a hindrance by ash incrustations.

A complete calculation of burning times must consider the possibility that the surface reaction rate will begin to control beyond a certain degree of combustion. Lack of data on the reactivity and configuration of combustion residues and the dependence of particle temperature upon an equilibrium with furnace surroundings make it inadvisable to attempt a general solution.

ELIMINATION OF ASH

Practical problems peculiar to the combustion of pulverized coal result almost entirely from the ash content. Ash may have an effect on combustion, and certainly it is a factor in radiation to furnace walls. The ash leaves the furnace as fly ash or collects as dry, pulverulent ash, as molten slag, or as more or less objectionable slag deposits.

The composition and properties of a representative ash sample are a useful guide but must be applied with care.[57] Physically separable portions of the coal ash have different properties. The composition and percentage of ash in individual coal particles vary within wide limits.[58] Bailey described the fly ash from hot furnaces as black, brown, gray, white, and transparent spheres together with unfused ash. An occasional coke particle had a number of ash beads on its surface.[31]

The molten beads may agglomerate either at the surface or in later collisions and may have sufficient fluxing action to absorb unfused ash. There is no simple relation between the size of the coal particle and the size or number of ash particles that result from its combustion. Investigations of fly ash[59] have failed to determine such a relation because they have not correlated the number and size distribution of the ash particles with the number and size distribution of the particular coal particles from which they were derived.

The histories of individual particles are just as varied as their compositions and sizes. Depending on its composition and temperature, an ash particle may remain molten for some time after complete burning. The temperature falls from a maximum which occurs while the particle is still burning. (Exceptions may occur for ash liberated from small particles or when an ash particle approaches a hotter burning particle.) The percentage of particles fusing below a certain temperature generally decreases with increased "coal-ash-fusion temperature." However, two coals having identical ash-fusion temperatures may behave differently. One might have a high percentage of medium-fusion-temperature particles, while the other might contain mostly high-fusion, together with a small but objectionable percentage of low-fusion, particles.

Unfortunately coal ash does not have a sharp melting point. Over a considerable

[57] Bailey, E. G., and Ely, F. G., *Trans. Am. Soc. Mech. Engrs.*, **63**, 465–71 (1941).

[58] Gould, G. B., and Brunjes, H. L., *Trans. Am. Inst. Mining Met. Engrs.*, **139**, 364–75 (1940).

[59] Dunn, J. T., *J. Soc. Chem. Ind.*, **45**, 60-1T (1926). Gibbs, W. E., *J. Inst. Fuel*, **3**, 361–9 (1930). Stern, A. C., *Combustion*, **4**, No. 12, 35–47 (1933). Hardie, P. H., *ibid.*, **6**, No. 9, 10–16 (1935). Olin, H. L., Smith, A. A., and Shaw, G. L., *ibid.*, **13**, No. 3, 37–9 (1941).

temperature range it may have a sticky, viscous consistency that leads to slag deposits. If allowed to accumulate, these deposits fall off and may damage the furnace floor. On boiler tubes they reduce heat transfer and may even stop the furnace draft. They are difficult to remove while the furnace is hot, and their removal requires considerable labor after the furnace is cooled. The formation of such deposits limits the capacity of furnaces designed for dry-ash removal. In slagging furnaces, there is always a band in which deposits tend to accumulate. This band is unavoidable since the temperature must vary from above the fusion point at the molten slag bed to a point below the fusion temperature of the lowest-melting particles at the boiler convection surface. To minimize and confine this band to a small region where it can be most easily removed is a problem of furnace design.

Ash samples collected from various parts of the same furnace do not have the same composition.[31, 57, 60] For example, ash or slag collected from the furnace bottom generally has more iron in a lower state of oxidation than the fly ash. Without detailed information on the individual furnaces, the cause of such segregation cannot be discussed except in general terms. Molten ash beads, having high density and minimum projected area, have comparatively high rates of fall through the furnace gases. However, the slag may be less fusible than the original coal ash. Ferrous oxide has more fluxing power than ferric oxide, but excessive reduction liberates metallic iron, leaving a less fusible slag. Certain ash constituents, specifically pyrites, owing to their low grindability, concentrate as coarse particles that fall to the furnace floor. Incomplete combustion of pyrites produces ferrous sulfide which collects as a liquid phase under the slag bed, often causing damage to tubes and cutting through floors.

Various criteria for ash fusibility have different significance, depending upon the type of furnace and the particular operating difficulty involved.[57] For dry-ash furnaces, the initial deformation under oxidizing conditions is important in relation to slag deposits. For slag-tap furnaces, the fluid temperature in a reducing atmosphere indicates the comparative ease of tapping. In the range between these temperatures, impingement on walls or boiler tubes should be avoided to minimize slag deposits requiring mechanical cleaning.

FURNACE TEMPERATURE AND HEAT TRANSFER

Owing to the heterogeneous nature of the furnace contents, there is no single physical quantity which represents the furnace temperature. Nevertheless, it is convenient to refer to relatively hot and cold furnaces without implying any quantitative differences unless specific directions for temperature measurement or evaluation are given.

Except for heat transfer to the furnace walls, the combustion products might attain the adiabatic temperature. This is the maximum equilibrium temperature that can be reached but does not limit the temperature at any given point in the furnace. A burning particle, being a source of heat, cannot be in equilibrium with its surroundings and might rise above the adiabatic temperature. The average gas temperature, in a volume receiving heat from its proportionate amount of fuel, would not be expected to do so.

In the absence of thermodynamic equilibrium, temperature is not a definable

60 Nicholls, P., and Reid, W. T., *Trans. Am. Soc. Mech. Engrs.*, **56**, 447–59 (1934).

quantity.[61] For instance, an endothermic chemiluminiscent reaction could take heat from the walls of a transparent vessel and transmit it to surroundings at the same temperature. An observer, having no knowledge of the reaction, would erroneously conclude that the vessel was hotter than its surroundings. Examining the contents of the vessel, he would find a temperature depending upon the relative ability of his thermometer to accept energy by conduction or by radiation. Under equilibrium conditions the relative population of all energy levels is determined by a single statistical parameter identifiable with temperature. Otherwise, it is necessary to consider the effect of the disturbed population and the heat-transfer process upon the probability of every conceivable transition. Only in this way is it possible to find a quantity approximating the attributes of temperature. Depending upon the displacement from equilibrium, the quantity found may vary for different applications.

The radiation from a small pulverized-coal flame contains bands ascribed to the presence of hydroxyl radicals.[62] These bands add slightly to the total radiation. However, it is best to consider the energy held by such groups as unliberated chemical energy. The chemical process controls their concentration and hence their rate of energy liberation. It would be extremely awkward to describe such processes in terms of temperature.

Most of the energy in the radiation from the small flame is distributed in a continuous spectrum marked by atomic lines. The line spectrum is controlled by the concentration and percentage of ash as well as by temperature. The distribution of energy in the continuous spectrum offers the best measure of temperature for the radiating particles. Difficulty in determining the opacity of the cloud and the energy in the line and band spectra makes the total energy unsatisfactory. Coppens' data,[62] by comparison with black-body radiation, indicate a temperature of about 2,000° C (3,632° F), but the uncertainty as to spectral sensitivity of his plates and optical system permits an error of several hundred degrees.

The radiation from large flames includes bands due to carbon dioxide and water in the combustion gases. The energy in these bands is determined by the depth of the gas layer, the gas composition, and temperature.[63] This radiation arises from transitions between the various vibration-rotation energy levels of the gas molecules. The relative populations of these levels are disturbed by the heat-transfer process. However, the efficiency of thermal collisions in re-establishing the distribution is probably such as to make the temperature, as defined by the kinetic energy of translation of the gas molecules, quite satisfactory for radiation calculations.

A thermocouple, in contact with a gas not at the same temperature as the surrounding walls, indicates a temperature depending upon the relative thermal and radiant heat-transfer coefficients. If the radiant coefficient is made comparatively small, as with the high-velocity thermocouple, the indicated temperature is that of the gas. With change in the relative coefficients, the temperature varies continuously to an opposing limit, depending, however, upon the radiant characteristics of the couple surface.

[61] Bennett, J. G., and Pirani, M., *J. Inst. Fuel*, **12**, 81-4 (1939). Tolman, R. C., *The Principles of Statistical Mechanics,* Clarendon Press, Oxford, 1938, 661 pp., see pp. 538–40.

[62] Coppens, L., *Ann. mines Belg.*, **40**, 149–69 (1939).

[63] Hottel, H. C., and Egbert, R. B., *Trans. Am. Soc. Mech. Engrs.*, **63**, 297–307 (1941).

The existence of such a limit suggests a radiation temperature defined by the integral

$$T_R{}^4 = \frac{1}{4\pi} \int_0^{4\pi} T_b{}^4 d\Omega \qquad (34)$$

where T_b is the temperature of a black body equivalent in total radiant energy to the sources seen in the solid angle $d\Omega$. Wohlenberg and Wise [64] proceeded directly to the calculation of heat transfer without determining the radiation temperature, but their procedure contains the essential steps needed for its calculation. It has the advantage in that it composes the effect of all radiation sources into a scalar function of position in space which is simply related to heat transfer. Thus, the rate of transfer to unit area of a black-body surface is given by the formula

$$R = 2\sigma(T_R{}^4 - T_b{}^4) \qquad (35)$$

The factor 2 enters because the radiation temperature at the surface is controlled throughout one hemisphere by the temperature of the surface itself.

The spectral distribution should be considered in calculating the radiation reaction with gases. For instance, thermal radiation shows light or dark bands depending upon whether an intervening gas layer is hotter or colder than a solid background. The absorption bands being a small part of the total spectrum, the radiation temperature, within the gas layer, varies slowly as compared to the temperature of the radiation capable of interacting with the gas. Whenever the radiation temperature effectively differs from the gas temperature, heat transfer occurs and either the gas temperature must change or heat must be conducted through the gas.

[64] Wohlenberg, W. J., and Wise, D. E., *ibid.*, **60**, 531–47 (1938).

In calculating heat transfer to a small isolated particle, such as a burning fuel or ash particle, it is convenient to use a radiation temperature based on the assumption that the given particle was not present. Since an individual particle makes a negligible contribution, except at distances of approach such that it occupies an appreciable solid angle, this procedure uses a radiation temperature T_r which errs only in failing to recognize the fine structure of the dust cloud.

Direct transfer of energy from particles to gas is of primary importance in maintaining the temperature distribution in the furnace.[64] The particle temperature must satisfy the equation

$$H = \lambda(T_p - T_g) + \psi(T_p{}^4 - T_r{}^4) \quad (36)$$

where λ and ψ are the appropriate heat-transfer coefficients, and H (equation 19), is the heat release at the particle surface. For ash, $H = 0$, the particle temperature must lie between the gas and radiation temperatures. For a burning particle, it rises to considerably higher values.

The distribution of energy in the furnace is best determined by calculation. Following a procedure analogous to that of Wohlenberg and Wise,[64] the radiation temperature can be calculated from tentative values for the gas, particle, and wall temperatures. Equation 36 and the requirement that the heat released must eventually be absorbed at the walls or contained in the combustion products leaving the furnace are then sufficient to calculate new temperatures. If these differ from the tentative values they may be used for repeated calculations until no further changes occur. The calculations are too laborious for routine application, but solutions for special cases are extremely valuable.

Wohlenberg and Wise made several approximations in order to reduce the prob-

lem to a readily soluble form. Actual temperatures were replaced by radiant mean temperatures for refractory walls, gas, burning coal, and ash particles. Each class of distributed radiators was replaced by an equivalent radiation source located at a radiant-mean position. This led to an error in the distribution of energy absorption at cold walls which was later corrected.[65] The radiation reaction with gas was calculated from the beam length and the radiant-mean gas temperature without regard to temperature gradients. A finite thermal conductivity was assumed between particles and gas, but the heat transfer to walls was assumed to be by radiation only. This was equivalent to an assumption that the gas had an infinite thermal conductivity except for a finite transfer coefficient between particles and gas and a zero coefficient between walls and gas.

As applied to a furnace having cold walls except for refractory at the burner end, the mean temperature of burning particles was found to exceed the mean gas temperature by about 1,000° F, while the ash was lower by 10 to 15° F. About 20 percent of the heat release was converted directly to radiation. The residue was stored in the combustion products from which about 30 percent was later converted into radiation.

Temporary storage of 30 percent of the heat release requires a large variation in gas and ash temperatures from the flame to the furnace outlet. Representing these temperatures by their mean values may introduce some error in the radiation calculations but probably does not invalidate the conclusions.

Within the flame, the average gas temperature is controlled by the percentage of the heat release not transferred directly to radiation. The burning particles, as heat

[65] Wohlenberg, W. J., *ibid.*, **61**, 263–6 (1939).

sources, must rise considerably above the gas temperature. Depending upon the relative influence of burning particles and the furnace walls, the radiation temperature may be above or below the gas temperature. Beyond the flame, heat transfer from a large mass of gas requires a radiation temperature below the gas temperature. Thermal conduction is important only within a few inches from the wall. In this region the gas temperature rapidly approaches the wall temperature, while the radiation temperature remains essentially constant and higher than the wall temperature by an amount related to the heat-transfer rate by equation 35.

The radiation temperatures shown in Fig. 20 were calculated from Bailey's data,[31] using 0.8 and the slag fluid temperature as the wall absorption coefficient and temperature, respectively. The hemispherical radiation temperature, as seen by the furnace wall, approximately follows the furnace outlet temperatures of Fig. 20. This is inverse justification for Bailey's assumption that the outlet temperature was a reasonable approximation to the effective radiation temperature of the primary furnace contents. The radiation temperature reflects the absorption rate and the slag fluid temperature, which is a function of coal characteristics as modified by ash segregation in the furnace. The inverted relation between adiabatic and slag fluid temperatures is either coincidental or a result of design and operating factors. Evidently, no simple relation exists between radiation and adiabatic temperatures which is not obscured by design and operating factors.

The radiation temperature rises above the wall temperature by an amount which depends upon the geometry of the furnace and the characteristics of the flame. The number of ash particles resulting from each

coal particle is a factor,[66] but is not subject to control. With a given coal and furnace, the particle-size distribution and the adiabatic temperature, hence the percentage of excess air, are the only obvious, controllable factors. In the absence of knowledge and methods for such control, the proportion of the heat release absorbed by radiant surfaces cannot be controlled except as the state of slagging and slag-fluid temperatures control the heat-receiving-surface temperatures.

Unburnt Carbon Losses

Combustible may escape from the furnace as gases or solids. Intensive mixing and moderate excess air in the presence of burning coal and incandescent ash particles are ideal conditions for the elimination of combustible gases. Such losses are usually negligible, and their occurrence generally indicates deficient air.

Combustible solids, approximating carbon in composition, may escape in slag or fly ash. Carbon is incompatible with molten slag containing oxides of iron, but considerable time may be required for its elimination. Carbon losses in molten slag are low but not necessarily negligible.[67] Fly ash always contains appreciable amounts of combustible. A survey by Jacobus and Bailey[68] indicated that the loss increased with high fixed carbon, coarse pulverization, cold furnaces, delayed mixture with air, low excess air, and high combustion rates.

The variables involved are so interconnected and so related to design and economy that general recommendations cannot

be made. Other things remaining constant, excess air varies inversely with furnace temperature. The heat release per unit volume may be higher in slagging furnaces where some flame impingement on furnace walls can be permitted. Thermal efficiency increases with fineness, but the pulverization cost also increases so that a certain fineness gives maximum economy.[69] Although the percentage retained on a 200-mesh screen may serve as an index of fineness, the performance of air-swept mills is such that the percentage on 100-mesh might be equally satisfactory without implying that either the coarse or the fine end of the size distribution is responsible for combustible losses.[68]

Evidence for a dependence of carbon loss upon ash content is significantly lacking except as resulting from an effect of slagging conditions upon furnace temperature. Some carbon may be occluded within ash particles. However, coal appears to be a heterogeneous substance with ash as the discontinuous phase. Bailey, examining fly ash from hot furnaces, found most of it as black, brown, gray, white, and transparent spheres together with unfused ash. An occasional carbon or coke particle had a number of ash beads on its surface.[31] Apparently molten ash does not wet a carbon surface. Without agglomeration into large masses, except at furnace walls, there is little opportunity for occlusion of carbon by ash.

Practical reduction of combustible losses results from an appropriate balance between burner design, furnace conditions, and fineness of pulverization. Aside from maintaining ignition, the burner, including contributory functions of the furnace, must insure that an adequate supply of air reaches all the coal. This may be accom-

[66] Wohlenberg, W. J., *ibid.*, **61**, 574–5 (1939).

[67] Bailey, E. G., and Hardgrove, R. M., *Proc. 3rd Intern. Conf. Bituminous Coal*, **2**, 349–69 (1931).

[68] Jacobus, D. S., and Bailey, E. G., *Proc. 2nd Intern. Conf. Bituminous Coal*, **2**, 241–75 (1928).

[69] Tenney, E. H., *Trans. Am. Soc. Mech. Engrs.*, **54**, FSP 54–7, 56–60 (1932).

plished at any point such that combustion is complete within the furnace. However, the period of rapid combustion leaves a residue containing a percentage of combustible that appears to depend upon the particle size. Continued combustion is limited by the high temperature coefficient of the surface reaction. If the furnace temperature is not high enough to overcome this chemical resistance, higher degrees of combustion cannot be attained.   .

Increasing fineness brings the heat release closer to the burner. The more rapid temperature rise of unignited particles produces less swelling in cenosphere formation. The net effect is an even smaller average size of burning particles which tend to approach more nearly to the gas than to the radiation temperature. In dry-ash furnaces, where cold walls produce low radiation temperatures, fine pulverization and intense combustion held close to the burners are the only available means for reducing combustible losses.

PRESENT STATUS AND DEVELOPMENT TRENDS

Many early applications failed because of an attempt to adapt pulverized coal to existing types of combustion equipment. Except fortuitously in such applications as the cement kiln, real progress has followed the inverse procedure of adapting combustion equipment to pulverized coal. The greatest development has been in large steam-boiler furnaces. High thermal efficiency demands low excess air and, consequently, furnace temperatures above ash-fusion temperatures. Water-cooled walls have minimized the destructive action of flame impingement and provided heat absorption to reduce the ash below its fusion temperature before reaching the narrow convection heating spaces.

The adaptability and limitations of the pulverized-coal flame are reasonably well known. Wherever high temperatures are desired and the effects of the coal ash are not prohibitively objectionable, the use of pulverized coal is generally possible and depends only upon questions of economy. Some advantage must be found to offset the cost of pulverization. The capital and operating costs of pulverization equipment may be less than the added cost of more expensive fuels. As compared to stokers, the use of pulverized coal is highly favored for units generating more than 100,000 pounds of steam per hour.[70] Equipment costs and the need for skilled operators prohibit its use in small units, below about 40,000 pounds of steam per hour.

Increasing usage of pulverized coal depends upon more efficient utilization of furnace volumes and the development of more reliable and less expensive methods of pulverization and combustion control. These problems must be considered as a unit. The amount of air blown through mills and classifiers affects both the size distribution and the amount of secondary air required at the furnace. The size distribution is an important factor in flame radiation. A shift towards smaller maximum but higher average sizes might give a more favorable distribution of burning particles, the most efficient radiators in the furnace.

70 Booth, R. D., *ibid.,* **61,** 81–7 (1939).

DIRECT GENERATION OF ELECTRICITY FROM COAL AND GAS (FUEL CELLS)

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The problem of converting the energy of solid fuels, such as coal, directly to electrical energy, without passing through the intermediate stages of conversion from thermal to mechanical and from mechanical to electrical energy, has, because of its industrial significance, attracted the attention of investigators for many years. It is easy to visualize the revolutionary effect which the development of a fuel cell might have upon our industrial life, not only from the standpoint of decreased cost of power, but particularly in mitigation of atmospheric pollution. Although all types of fuel cells which have been proposed so far have been unsuccessful, there is continued interest in the problem.[1]

The recovery of the energy in carbon or in fuel of high carbon content, such as coal, as electrical energy may theoretically take place either by *direct* utilization of the principal reactants—carbon and oxygen—in a cell, or *indirectly* by use of certain of their reaction products. Fuel cells may, therefore, conveniently be classified into two broad types, direct and indirect.

[1] See, for example, a review by E. Baur and J. Tobler, *Z. Elektrochem.*, **39**, 169–80 (1933), and U. S. Pats. 1,963,550 (1934) and 2,175,523 (1939) issued to H. H. Greger.

DIRECT CELLS

The maximum electrical energy which can be obtained from the reaction $C + O_2 \rightarrow CO_2$ can be calculated from the free energy change involved; it amounts to 109.4 watt-hours per gram atom of carbon, or 4.136 kilowatt-hours per pound. The effect of changes in temperature, and of the pressure at which the oxygen is supplied, can also be predicted from the effects of changes in these variables upon the magnitude of the free energy change. The voltage of a cell in which graphitic carbon reacts with oxygen at 1 atmosphere and at 25° C is given by the following relation:

$$\frac{\Delta F^{\circ}_{298} \times 4.18}{NF} = E_{298}$$

where ΔF°_{298} is the free energy change, $-94,260$ calories;[2] 4.18 is a constant relating calories and watt-seconds; N is the number of unit charges involved in the reaction, 4 in this case; F is the quantity of electricity associated with unit charge, 96,494 coulombs, and E_{298} is the voltage of the cell, 1.01. It can be shown[2] that the effect of temperature on the voltage of the

[2] Lewis, G. N., and Randall, M., *Thermodynamics*, McGraw-Hill Book Co., New York, 1923, p. 576.

cell will be very slight since the value of ΔF at 1,000° differs by only 16 calories from that at 25° C.

The effect of changes in the partial pressure at which the oxygen is supplied can be calculated from the relation [3] $F - F° = RT \ln a$, where F is the free energy in any chosen state, $F°$ is the free energy in the standard state, a is the activity—unity for a perfect gas at 1 atmosphere—and R and T have their usual significance. It can be shown from the above relation that, with oxygen supplied at 10 atmospheres, the value of ΔF_{298} is increased by 1,360 calories and the electromotive force of the cell by 0.014 volt. If air, in which the oxygen partial pressure is approximately 0.2 atmosphere, is used in place of oxygen, the value of E_{298} will be decreased by approximately 0.010 volt and the value of $E_{1,273}$ by about four times this amount. Thus, it is evident that considerable changes neither in temperature nor in the partial pressure at which the oxygen is supplied will affect the voltage of such a fuel cell markedly.

If we are to obtain the energy of the reaction $C + O_2 \rightarrow CO_2$ from the electrochemical reaction of carbon and oxygen, these elements must function as the electrodes in a cell and each must acquire a charge, either by sending ions into the electrolyte or by the discharge of ions from the electrolyte. Examples of both types of behavior are common among the elements. For example, a zinc electrode immersed in an electrolyte becomes charged negatively by sending positively charged zinc ions into solution. The iron electrode in an Edison cell becomes negatively charged by discharge of hydroxyl ions, and a gaseous, nonconducting element like chlorine, adsorbed on the surface of a noble metal, dissolves as negatively charged chloride ions

and leaves the noble metal positively charged. Unfortunately, carbon, so far as we know, never ionizes, and oxygen does so only slowly, after activation under special conditions, such as at the surface of a finely divided noble metal or at specially active carbon surfaces. Both carbon and oxygen can function electromotively, however, by reaction with ions from the electrolyte, but the process is usually slow. Because of simplicity and directness, this type of fuel cell appealed to many of the early investigators, and various cells based upon this principle have been described and patented. It has since been shown that the action of some of the cells was really dependent upon the formation of an active secondary product; for example, it has been demonstrated [4] for cells in which the carbon was immersed in fused alkali that it is the hydrogen formed by reaction of the carbon with the alkali which is electromotively active, and that the carbon really functions as a hydrogen electrode and is not charged directly by discharge of OH′. For simplicity, however, all cells which have used carbon as the negative electrode and in which the secondary product, if any, is formed directly in the cell have been classified as "direct." [5]

Cells of this direct type have operated either at ordinary temperatures with aqueous electrolytes, or at elevated temperatures, making use of fused electrolytes or aqueous electrolytes under pressure. Often either platinum, iron, nickel, silver, copper, or some oxide has been employed as the cathode, and since the potentials of the electrodes have not been studied independently it is difficult to decide whether the limitations of the cell have been due to the

3 See p. 255 of ref. 2.

4 Haber, F., and Bruner, L., *Z. Elektrochem.*, 10, 697–713 (1904).

5 For other classifications see, for example, ref. 41 and Baur and Tobler's review, ref. 1.

low reactivity at the carbon or at the oxygen electrode. The activation of oxygen is discussed in later sections.

Early cells of the direct type were those of Becquerel [6] and of Jablochkoff,[7] in which platinum or iron cathodes and carbon anodes were used in combination with an electrolyte of fused potassium nitrate. Obviously these cells erred in the use of carbon in direct contact with an oxidizing agent, and furthermore a very expensive form of "fuel," electrode carbon, was necessary. Cells of this type have been described by a number of workers.[8, 9, 10]

An improvement in the Becquerel-Jablochkoff type of cell was made by the replacement of the oxidizing electrolyte by alkali carbonate or hydroxide.[11] Jacques [12] built a cell of this type and claimed a current of 150 amperes at 1 volt from a battery 50 centimeters long by 8 centimeters in diameter. A test by Stone & Webster, Inc., was reported [13] which showed the cell to operate with 82 percent of the theoretical efficiency. This cell received considerable attention from the popular press [11] and was pictured (Fig. 1) as a device which could be placed in the basement of domestic dwellings to furnish current for the household. This hope, of course, was never

realized.   During the following decade studies on the Jacques cell and its modifications were made by many workers.[15]
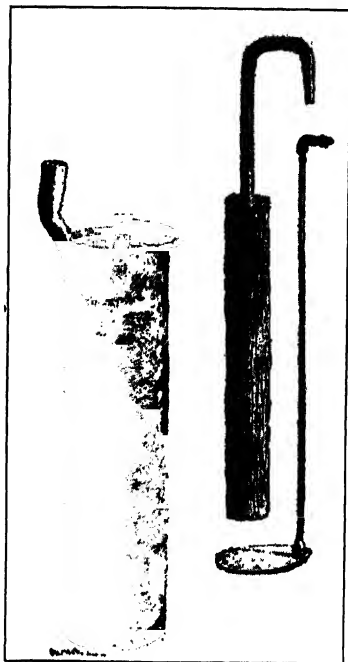
FIG. 1.   Jacques' cell.[14]   "Taken apart to show iron pot, stick of carbon with iron suspension, and air-supply pipe with rose nozzle. This carbon is twenty inches long and ten inches in circumference, and yields a current of about one hundred and fifty amperes. The electromotive force is one volt."

Haber and Bruner,[16] as a result of an investigation of the Jacques cell, reached the important conclusion that a carbon electrode immersed in alkali at elevated tem-

6 Becquerel, A. C., *Traité d'électricité et du magnétisme*, Firmin Didot Frères, Paris, 1855, Vol. I, pp. 183, 185.

7 Jablochkoff, P., *Compt. rend.*, 85, 1052–3 (1877).

8 Brard, M., *Compt. rend.*, 95, 890–2, 1158–60 (1882). Shrewsbury, C. P., Marshall, F. L., Cooper, J., and Dobell, J. L., *J. Soc. Chem. Ind.*, 14, 974 (1895).

9 Korda, D., *Elektrotech. Z.*, 16, 272 (1895).

10 Schmitz, G., *ibid.*, 16, 145 (1895).

11 Archereau, H. A., Brit. Pat. 1,037 (1883). Anon., *Z. Elektrochem.*, 4, 129–36, 165–71 (1897). Fabingi and Farkas, *Compt. rend.*, 106, 1597–8 (1888).

12 Anon., *Z. Elektrochem.*, 4, 129–36, 165–71 (1897).

13 Editorial, *Elec. Eng.*, 21, 261, 497 (1896).

14 Jacques, W. W., *Harpers Magazine*, 94, 144–50 (1896–7).

15 Reed, C. J., *Elec. World*, 28, 44–5, 74–5, 98–100, 134–5 (1896). Liebenow, C., and Strasser, L., *Z. Elektrochem.*, 3, 353–62 (1897). Sacher, J., and Lorenz, R., see p. 852 of ref. 18. Byrnes, E. A., *Trans. Electrochem. Soc.*, 2, 113–9 (1902). Lorenz, R., see ref. 9.

16 See p. 703 of ref. 4.

peratures really constitutes a hydrogen electrode owing to the presence of active hydrogen formed by reaction between the alkali and either carbon itself or carbon monoxide, and that the potential of the carbon depends upon the velocity of hydrogen formation. The iron electrode was shown to function as an oxygen electrode after reaching the passive state. Haber believed that the passivity was brought about by small amounts of manganate in the alkali. The suggested reactions were as follows:

$$MnO_4'' + H_2O + 2e \rightarrow MnO_3'' + 2OH'$$
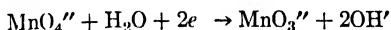
MnO_3'' was reconverted to MnO_4'' by the action of air.

Taitelbaum [17] used carbon and iron electrodes immersed in molten sodium hydroxide at 370 to 390° C. Manganese dioxide was added to the melt around the iron electrode to facilitate maintenance of the oxygen potential and various reducing agents, such as carbon monoxide, hydrogen, carbon, sawdust, and petroleum, were added at the carbon electrode. With a carbon electrode alone, 4 centimeters in diameter by 8 centimeters long, the cell furnished a current of 0.020 ampere at 0.53 volt. Better results were obtained with certain additional combustible depolarizers. Sawdust gave as high as 0.100 ampere at 0.50 volt. Less satisfactory results were obtained with petroleum, carbon monoxide, sugar, hydrogen, and naphthalene as reducing agents.

Bechterew [18] investigated the potential of carbon (Lampenkohle) up to 650° C in a number of electrolytes.

Baur and Ehrenberg,[19] using a carbon anode, fused borax electrolyte, and oxygen dissolved in molten silver as the oxygen electrode reported currents of 1.0 ampere per square decimeter at 1 volt. They also stated that a current density of 5.0 amperes per square decimeter can be used with a polarization of only 20 percent. Analysis of the data shows that the value, 5.0 amperes per square decimeter, is too large by a factor of 10.

Fischer and Lepsius [20] constructed a cell consisting of a carbon and a magnetite electrode, the former 1.0 centimeter in diameter, the latter 1.5 centimeters, immersed in molten sodium hydroxide. On open circuit at 550°, the electromotive force was 0.8 volt; when closed through 10 ohms an approximately constant current of 0.060 ampere at 0.6 volt was observed.

Hofmann and Ritter [21] worked with an aqueous electrolyte system. The carbon anode was immersed in $2 N$ NaOH and a platinum cathode in 20 percent sodium hypochlorite. The two half-cells were connected by a sodium chloride bridge. The theoretical voltage was calculated to be 1.3; the observed voltage on open circuit was 0.9 volt. In experiments where current was drawn from the cell through a silver coulometer and the amount of carbon dioxide evolved was determined, the theoretical relation was found. Thiel [22] discussed the theory of this cell. The cost both of the "fuel" and of the oxidant renders this cell impractical.

Baur, Petersen, and Füllemann [23] studied the electromotive force of various metal oxide-carbon cells at 700 to 1,300° C with molten borax as an electrolyte. The ob-

[17] Taitelbaum, I., Z. Elektrochem., 16, 286–300 (1910).

[18] Bechterew, P., Z. Elektrochem., 17, 851–77 (1911). A survey of the literature up to 1910 is included.

[19] Baur, E., and Ehrenberg, H., ibid., 18, 1002–11 (1912).

[20] Fischer, Franz, and Lepsius, R., Ber., 45, 2316–7 (1912).

[21] Hofmann, K. A., and Ritter, K., ibid., 47, 2233–44 (1914).

[22] Thiel, A., Z. Elektrochem., 21, 325–9 (1915).

[23] Baur, E., Petersen, A., and Füllemann, G., ibid., 22, 409–14 (1916).

served electromotive forces were found to be a function of the dissociation pressure of the oxide system.

Reed [24] constructed a simple cell from fireclay crucibles (Fig. 2). A graphite grid anode floated on the electrolyte in the inner compartment and was covered with crushed

was effective at both electrodes, being alternately oxidized by contact with air at the cathode to MnO_4'' and reduced by electrochemical discharge, while at the anode the reverse reactions took place, the reduction being chemical, by contact with the carbon, and the oxidation electrochemical.
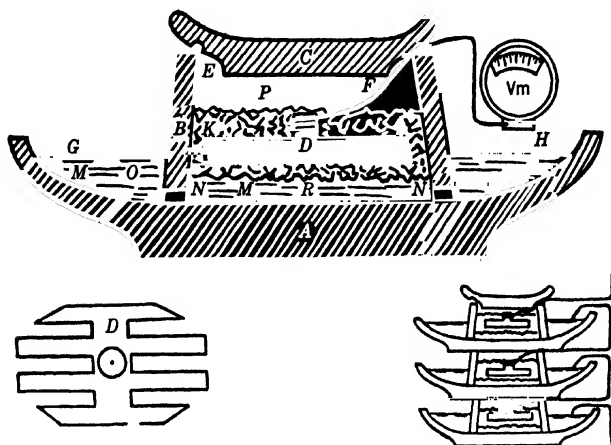
Fig. 2. Reed's cell.[24] "A—Six-inch Battersea roasting dish. B—Section of three-inch (7.5 cm.) Battersea crucible. C—Cover. D—Graphite electrode. E—Aperture for escape of products of combustion. F—Wire conductor to voltmeter. G—Gold foil electrode. H—Wire conductor to voltmeter. K—Broken coal. M—Fused borax with oxides of manganese in solution. N—Communication passages. O—Oxidizing region. P—Waste gas chamber. R—Reduction region."

electrode carbon. The gold-foil cathode floated on the surface of the melt in the outside compartment in free contact with air. The electrolyte consisted of a mixture of borax and manganese dioxide, and the cell operated at 935 to 990° C. The open-circuit electromotive force was 0.9 volt, which, after delivering 0.171 ampere for an hour, fell to 0.82. The anode area was about 50 square centimeters, and the cathode 87 square centimeters. Allemand [25] has suggested that the manganese dioxide

Baur, Treadwell, and Trümpler's [26] cell consisted of a magnetite-ferric oxide cathode separated by a magnesium oxide diaphragm from the carbon anode, which was immersed in a melt of mixed sodium and potassium carbonates. The fused electrolyte in the pores of the diaphragm furnished the conduction but, according to the patent specification, did not wet the surface of the oxygen electrode, which was kept in the oxidized state by a current of air. No data on the performance of this cell were given, but the estimated capacity was 470 watts per cubic meter.

24 Reed, S. A., *Trans. Electrochem. Soc.*, **33**, 89–94 (1918).

25 Allemand, A. J., and Ellingham, H. J. T., *Principles of Applied Electrochemistry*, Longmans, Green & Co., New York, 1924, p. 228.

26 Baur, E., Treadwell, W. D., and Trümpler, G., *Z. Elektrochem.*, **27**, 199–208 (1921).

The two cells of Fischer and Krönig [27] represent an attempt to operate a fuel cell at higher than atmospheric pressure and were apparently an outgrowth of work on pressure oxidation of carbonaceous materials. In the second design, which gave the more satisfactory results, the inside of a small steel autoclave constituted the cathode surface. The anode was a small iron rod, which was kept in the reduced state by a suspension of brown coal, confined to contact with the anode by a porous cup. An aqueous alkaline electrolyte was employed. The iron anode was insulated electrically from the autoclave top, and the whole system was operated at pressures up to 30 atmospheres of air at 200° C. Under these conditions, the electromotive force on open circuit was approximately 0.55 volt. This rapidly fell to zero, no doubt owing largely to diffusion of the "humates" formed by oxidation of the brown coal through the porous cup into contact with the cathode.

Von Rhorer's [28] cells used anodes of either coke, retort carbon, or lamp carbon, held in position at the bottom of the cell by an iron conductor insulated with a porcelain shield, or of ground coal confined in an iron spoon. The cathodes were platinum, silver, copper, or iron, part of the electrode being in direct contact with the air. The cell was operated at 900° C, and the electrolyte consisted of a mixture of sodium and potassium carbonates to which varying amounts of barium carbonate, magnesium oxide, and aluminum oxide were added. The open-circuit electromotive force of these cells was approximately 1.2 volts, and it was concluded that the chief process was the oxidation of carbon to carbon monoxide. In prolonged experiments, during which the carbon anode material was completely consumed, the current efficiency at the carbon was only about 40 percent, the losses due to chemical combustion being high. Tests run on the cells under load with a cell voltage of approximately 0.8 showed around 16 percent energy efficiency on the total carbon consumed. On the basis of that consumed electrochemically, the efficiency reached 40 percent.

Since 1930 few investigations on the direct type of fuel cell have been reported. Sconzo [29] studied the potential of a cell consisting of carbon and silver electrodes immersed in an electrolyte of fused silver nitrate at temperatures up to 350° C. Up to approximately 240° C, the carbon functioned as the cathode, the oxygen electrode. Reversal was noted above this temperature. Tamaru [30] and coworkers studied cells consisting of charcoal cathodes and platinum, palladium, gold, silver, or copper anodes. A eutectic mixture of potassium carbonate, sodium carbonate, and lithium carbonate was found useful in the range 400 to 550° C. Measurements of single electrode potentials showed that polarization was serious at both electrodes at 400 to 500° C, but at 550 to 600° C it was chiefly the oxygen electrode which functioned poorly. Manganate was found to improve the performance when platinum, palladium, gold, or silver cathodes were employed. Borate was found to be an especially useful addition agent with copper cathodes.

[27] Fischer, Franz, and Krönig, W., *Ges. Abhandl. Kenntnis Kohle*, **7**, 213–30 (1922–3).

[28] Von Rhorer, L., *Z. Elektrochem.*, **29**, 478–88 (1923).

[29] Sconzo, A., *Ann. chim. applicata*, **22**, 794–802 (1932).

[30] Tamaru, S., and Kamada, M., *Z. Elektrochem.*, **41**, 93–6 (1935); *J. Chem. Soc. Japan*, **56**, 92, 103 (1935).

INDIRECT CELLS

By far the greater number of fuel cells which have been proposed are of the indirect type. Although the difficulties with ionization of the carbon, with its sluggish kinetic behavior, and with the accumulation of inorganic impurities from the ash present in solid commercial fuels, may be largely eliminated by making use inside a cell of reaction products of coal prepared in a separate chemical reaction outside of the cell, care must be exercised in choosing this reaction, or a significant fraction of the energy available from the original oxidation of the carbon will be lost and the whole point of the fuel cell disappears.

For example, it has been proposed to build a gas cell using carbon monoxide, prepared in a gas producer, as the reducing agent. The cell reaction would be $CO + \frac{1}{2}O_2 \rightarrow CO_2$, and the free energy change, at 25° C, $-61,750$ calories,[2] but even if this cell operated at 100 percent efficiency we could recover only 65.5 percent of the energy in the original carbon. It would have the advantage of a somewhat higher voltage than a cell based on the oxidation of carbon to carbon dioxide: 1.33 compared to 1.01 volts. At higher temperatures, however, the free energy change of this reaction decreases rapidly so that a cell operating on producer gas at 1,000° C, at 100 percent efficiency, would recover only 43.3 percent of the energy of the original oxidation of the carbon to carbon dioxide, and the theoretical cell voltage would only be 0.882 volt.

An example of an especially poorly chosen reaction is the proposal to use the carbon to reduce sulfur trioxide to sulfur dioxide, $2SO_3 + C \rightarrow 2SO_2 + CO_2$, and to carry out the oxidation of the sulfur dioxide to sulfur trioxide in a cell, thus furnishing an amount of electrical energy equivalent to the free energy change available in the oxidation of sulfur dioxide to trioxide. The free energy change for the reaction $2SO_2 + O_2 \rightarrow 2SO_3$ is, however, but $-32,460$ calories [31] at 25° C so that only 34.5 percent of the energy available by oxidation of the original carbon could be recovered as electrical energy. This figure for efficiency is only slightly higher than that of the best steam plants.[32] Thus, it is evident that, if the carbon is to be put through some chemical reactions outside of the cell, they must proceed with small free energy changes if a high overall efficiency is to be attained.

From this standpoint the reaction of carbon with steam, which may be typified by the equation $C + H_2O \rightarrow CO + H_2$, is satisfactory. This is an endothermic reaction, and the hydrogen and carbon monoxide formed, if burned in a fuel cell at 100 percent efficiency at room temperature, would yield the equivalent of 116,000 calories in electrical energy.[33] Thus, from the energy relations, a cell operating on water gas would appear to have possibilities. Present costs of gasification are, however, such that energy in the form of water gas is several fold as expensive as that in the form of coal, so that, even if very high efficiencies are assumed for the fuel cell, the resulting electrical energy will still be more costly than that produced by the much less efficient steam plant.

Indirect fuel cells have been proposed which operate with gaseous, dissolved, or solid reaction products of carbon. The temperatures of operation have varied from

31 See p. 551 of ref. 2.
32 Efficiencies of 35 percent have been reached with mercury boilers: *Elec. World*, **97**, 918 (1931); *Combustion*, **11**, No. 7, 33 (1940); see also *Energy Resources and National Policy*, Government Printing Office, Washington, 1939, pp. 108–9.
33 See pp. 485 and 576 of ref. 2.

room temperature up to 1,100° C. The various types are discussed in the following paragraphs.

CELLS OPERATING ON GASEOUS REACTION PRODUCTS

Over a hundred years ago Grove [34] observed that there was a difference of potential between platinum electrodes if one was saturated with hydrogen and the other with oxygen and that a certain amount of energy could be drawn from such a cell. This constitutes the first record of a gas battery. Several hydrogen-oxygen fuel cells have been patented.[35] Mond and Langer [36] constructed an elaborate hydrogen-oxygen cell. The electrodes consisted of thin platinum sheets perforated with some 1,500 small holes per square centimeter. To decrease internal resistance the sheets were backed with lead strips provided with copper leads, and to increase reactivity they were coated with platinum black. The electrolyte consisted of dilute sulfuric acid absorbed in a porous diaphragm of gypsum, asbestos, or cellulose board. The electrodes were clamped against the two sides of the diaphragm saturated with the electrolyte, and the whole was assembled in a hard-rubber frame. Inlet and outlet tubes were provided for hydrogen and for oxygen back of the electrodes. The electromotive force of such a battery was found to be dependent upon the method of preparation of the platinum black; the highest observed was 0.97 volt. Currents of 2 to 2.5 amperes at 0.73 volt (1.45 to 1.82 watts) could be drawn from a battery of active surface of 700 square centimeters,

containing 0.35 gram of platinum foil and 1.0 gram of platinum black. The energy efficiency based on hydrogen consumed was approximately 50 percent. Heat was dissipated and the operating temperature was maintained at about 40° C by blowing an excess of air around the oxygen electrode. This current of air also served to carry off the water formed in the reaction. The cell showed strong concentration polarization due to accumulation of SO_4'' and HSO_4' at the anode and water at the cathode, resulting in a decrease of the electromotive force of 4 to 10 percent per hour of operation. This polarization was overcome by reversing the flow of the gases. The high initial cost, small energy output per unit of volume, low efficiency, and high-priced "fuel" required, among other factors, rendered this cell entirely impractical. Wright and Thompson [37] developed independently a similar type of cell.

Cailletet and Collardeau [38] studied the effect of pressure on the capacity of hydrogen electrodes of spongy platinum, gold, and palladium. At 580 atmospheres they estimated the capacity of spongy platinum at approximately 56 ampere-hours per kilogram. Siegl [39] made use of platinized carbon granules and claimed greatly increased capacity over platinum alone. Gaiser [40] added colloidal platinum or silver.

Rideal and Evans [41] used nickel as a support for the platinum black in a hydrogen-oxygen cell without success. Hofmann [42] made a study of the hydrogen-oxygen cell using platinized clay tubes as electrodes.

[34] Grove, W. R., *Phil. Mag.,* **14,** 127–30 (1839).
[35] Blanchard, V. W., U. S. Pat. 268,174 (1882). Müller, W. A., and Wellman, J. F., Ger. Pat. 99,544 (1898). Zöpke, O., Ger. Pat. 131,596 (1902).
[36] Mond, L., and Langer, C., *Proc. Roy. Soc.* (*London*), **46,** 296–308 (1889).

[37] Wright, A., and Thompson, C., *Proc. Roy. Soc.* (*London*), **46,** 372–6 (1889).
[38] Cailletet, L., and Collardeau, E., *Compt. rend.,* **119,** 830–4 (1894).
[39] Siegl, K., *Elektrotech. Z.,* **34,** 1317 -8 (1913).
[40] Gaiser, C., Ger. Pat. 346,771 (1922).
[41] Rideal, E. K., and Evans, U. R., *Trans. Faraday Soc.,* **17,** 466–84 (1921).
[42] Hofmann, K. A., *Ber.,* **56,** 1456–63 (1923).

Foerster [43] studied a hydrogen-chlorine cell with a platinum anode and carbon cathode, using dilute hydrochloric acid as the electrolyte. Currents up to 1 ampere per square decimeter could be obtained with little polarization. Polarization at the hydrogen electrode was the limiting factor determining the current density. Carbon was found unsatisfactory as a carrier for the platinum black. Schmid [44] studied the impregnation of porous carbon with platinum. Hydrogen was introduced from the inside of the porous structure and bubbled out through the pores. Such *Diffusiongaselektrode* showed satisfactory behavior up to current densities as high as 2 amperes per square decimeter and represented a very definite advance. Bührer and Regensburger [45] studied the action of porous carbon electrodes impregnated with rare metals. Waldburger [46] has investigated the poisoning of platinized carbon electrodes. Tobler [47] studied the behavior of nickel, platinized nickel, iron, platinized iron, platinized graphite, and platinized platinum. Only the electrodes containing platinum functioned, and they did not yield constant results over any considerable time unless great care was taken to purify the hydrogen. Platinized graphite electrodes could be operated at 0.7 ampere per square decimeter with 0.1 volt polarization.

The gas cells discussed in the preceding paragraphs utilized hydrogen as a fuel and operated at room temperature. Even less success has attended the efforts of investigators to activate carbon monoxide. Wi-

nand,[48] Borchers,[49] and Hofmann and co-workers [50] have constructed cells using copper anodes and carbon monoxide as the reductant. Except in the Hofmann cell, there is no evidence that the small electromotive force observed was actually due to the oxidation of carbon monoxide, and the Hofmann cell polarized very easily. Acetylene and other gaseous hydrocarbons have been suggested as reductants in a fuel cell,[51] but no experimental data are available.

Cells using sulfides and sulfurous acid have been proposed.[52] Reed,[15] in his discussion of the problem, suggested a cell operating on sulfur dioxide and hydrogen sulfide.

The great difficulty of obtaining electromotive activation of hydrogen, carbon monoxide, and other gaseous reaction products of carbon at ordinary temperatures has been indicated in the preceding paragraphs. Naturally, reaction rates increase at elevated temperatures, and a large number of cells have been proposed to operate in the 500 to 1,000° C range. The earlier of these cells used antimony, tin, or lead anodes with hydrogen, carbon monoxide, or illuminating gas and molten oxides or salts as electrolyte.[53, 54] Cells with copper anodes, using carbon monoxide or gaseous hy-

[43] Foerster, F., *Z. Elektrochem.*, **29**, 64–79 (1923).

[44] Schmid, A., *Helv. Chim. Acta*, **7**, 570–3 (1924).

[45] Bührer, C., dissertation, Basel, 1930. Regensburger, dissertation, Karlsruhe, 1929.

[46] Waldburger, E., dissertation, Basel, 1930.

[47] Tobler, J., *Z. Elektrochem.*, **39**, 148–67 (1933).

[48] Winand, P., *Elektrotech. Z.*, **16**, 35–6 (1895).

[49] Borchers, W., *Chem. Ind.*, **17**, 502–5 (1894).

[50] Hofmann, K. A., *Ber.*, **51**, 1526–37 (1918), **53**, 914–21 (1920). Hofmann, K. A., and Wurthmann, B., *ibid.*, **52**, 1185–94 (1919).

[51] Union Elektricitäts Gesellschaft, Ger. Pat. 142,227 (1902).

[52] Tourneur, H., Fr. Pat. 332,982 (1903). Basset, L., Brit. Pats. 16,905 (1906), 21,475 (1907).

[53] D'Arsonval, A., Fr. Pat. 152,348 (1882). Atkinson, L. B., and Treharne, F. G., Brit. Pat. 8,906 (1896). Dobell, J. L., Brit. Pat. 2,272 (1897). Rawson, W. S., Brit. Pat. 24,570 (1898).

[54] Mugdan, M., *Chem.-Ztg.*, **26**, 1156 (1902).

drocarbons, have also been described.[55, 56] Citovick's cell was intended to serve as a secondary gas battery.

Cells with nickel or iron anodes, employing carbon monoxide or hydrogen or mixtures of these gases, and using for electrolyte molten alkali carbonates with or

Treadwell, and Trümpler [60] (Fig. 3), which used iron wire anodes in the form of clippings and granular magnetite cathodes confined in channels in a magnesium oxide block. The cathode was kept in the oxidized state by a current of air and the anode in the reduced state by hydrogen or
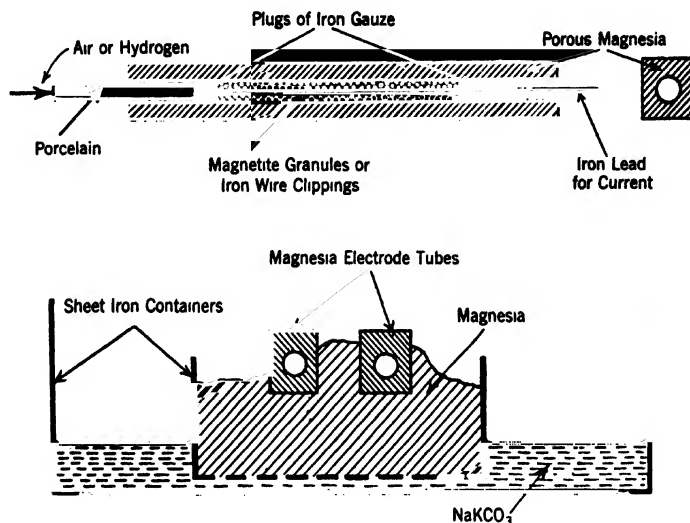
FIG. 3. Baur's cell.[58]

without additions of borates and/or halides, have been studied by many investigators.[57, 58, 59, 60] Outstanding in these investigations are the studies of Baur and his coworkers which extend over many years. Typical of these is a cell described by Baur,

carbon monoxide. The electrolyte consisted of a mixture of fused potassium and sodium carbonates which filled the capillaries of the magnesium oxide and permitted conduction between the electrodes without wetting them. The operating temperature was 800 to 900° C. It is difficult to estimate current densities in these cells, but they probably did not exceed 1.0 ampere per square decimeter at 0.5 to 0.7 volt.

Greger [61] has described similar types of cells making use of granular or wire elec-

[55] Hoffmann, A. G., Ger. Pat. 369,829 (1923).
[56] Hoffmann, F., Ger. Pat. 437,009 (1926). Citovick, E. R., Brit. Pat. 303,027 (1929).
[57] Bucherer, A. H., Z. Elektrochem , 3, 192–3 (1896).
[58] Haber, F., Z. anorg. Chem., 51, 356–68 (1906). Beutner, R., Z. Elektrochem., 17, 91–3 (1911). Baur, E., and Ehrenberg, H., ibid., 18, 1002 (1912). See also p. 412 of ref. 23.
[59] Baur, E., Helv. Chim. Acta, 4, 325–33 (1921) ; Ger. Pat. 357,290 (1921).
[60] See p. 204 of ref. 26.

[61] Greger, H. H., Proc. World Eng. Congr. Tokyo, 1929, 32, 195–205 (1931) ; Ger. Pat. 570,-600 (1933).

trodes packed into channels or cylindrical openings in a magnesium oxide block. The operating temperature was lower than that of Baur's cells, 600° C, owing to the use of a special low-melting electrolyte, consisting of alkali and alkali-earth carbonates with alkali halides and barium chloride. Special advantages were claimed for cathodes consisting of chrome nickel steel granules or of artificial ferrites of the general structure $MeO \cdot Fe_2O_3$, where Me may be copper, magnesium, zinc, or nickel, and where the ratio of MeO to Fe_2O_3 may range from 0.5 to 1.5. As in Baur's cell, saturation of the magnesium oxide block with the fused electrolyte provides the conducting path between the electrodes. Nearly theoretical voltages were obtained on open circuit, and the cell furnished 0.115 ampere at 0.8 volt. On the basis of the apparent superficial area of the electrodes, this corresponded to a current density of about 0.2 ampere per square decimeter.

Cells using platinum anodes and carbon monoxide or hydrogen have been employed for theoretical studies.[62] Haber and co-workers devised small gas cells operating at elevated temperatures with glass or porcelain electrolytes and using platinum electrodes and carbon monoxide as the fuel. Satisfactory theoretical values of electromotive force were obtained for the reactions involved, but the cells polarized at low current densities.

Because of the high rates of diffusion of hydrogen in palladium at elevated temperatures, cells with palladium anodes have been of special interest.[63, 64] Koenig used a U-shaped, thin-walled, tubular electrode of palladium immersed in a mixture of

fused potassium and sodium nitrites. Hydrogen gas passed by diffusion from the inside of the electrode to the electrode-electrolyte interface. Operating at 250° C, the open-circuit voltage was 0.75, and at a current density of 0.7 ampere per square decimeter the electromotive force was constant at 0.5 volt.

Even at elevated temperatures all investigators working with gaseous fuels have encountered the problem of getting satisfactory reaction rates between the gas and the electrode at the electrolyte-electrode interface. In attempts to obviate this difficulty, electrode areas have been greatly increased by the use of special mechanical designs or of finely divided, porous, or granular electrode materials. Diffusion through a thin-walled metal electrode appears sound theoretically, but as yet no one has demonstrated a sufficiently high rate of diffusion and activation.

Since the time of Grove [34] it has been established that at ordinary pressures activation takes place only at dry solid surfaces, owing, no doubt, to the general tendency of liquids to displace adsorbed gases from the activating surface. Baur [65] described a proposal to solve the problem by discontinuous operation. The dry electrode was allowed to react with the gas and then immersed in the electrolyte, the power was withdrawn, and the polarized electrode was removed, dried, and reactivated, and so forth. Mond and Langer [36] attempted to avoid the difficulty by retaining the electrolyte in a porous block but encountered serious concentration polarization. Schmid [44] used a so-called *Diffusiongaselektrode*, where the gas is introduced from the inside of a porous structure and where through regulation of the gas pressure the entrance of the electrolyte into the pores of

62 Haber, F., and Moser, A., *Z. Elektrochem ,* **11**, 593–609 (1905).

63 Beutner, R., *ibid.*, **17**, 91–3 (1911).

64 Koenig, A., *Siebert Festschr.*, **1931**, 179–92 ; *Chem. Abs.*, **26**, 4259 (1932).

65 See Baur, E., and Tobler, J., p. 173 of ref. 1.

the electrode is hindered. Baur [65] pointed out, however, that it has been shown that, finally, wetting and inactivation take place even with this construction. The use of an electrolyte in gelatinized form or of a

special carbon containing pores which are impermeable to liquid molecules but are still readily permeable to gases.

An interesting contribution toward the solution of the problem has been made by
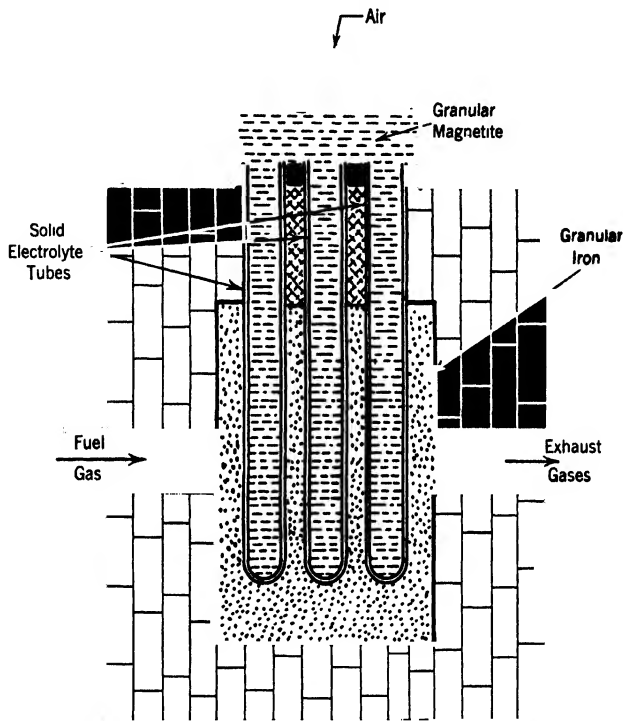
FIG 4   Baur's cell with solid electrolyte.[70]

gelatinous electrolyte layer over the electrode has likewise been suggested. As would be expected, concentration polarization is also very severe with such constructions. A layer of material such as paraffin, zinc soaps, resins, or lacquers over the electrode to permit the passage of gases and ions, but not of liquid molecules, has been proposed.[66]   Jungner [67] recommended a

Baur and coworkers.[68, 69, 70]   Baur proposed to avoid the difficulties of wetting by the use of a cell operating at high temperatures with a solid electrolyte. Such

[66] See Baur, E., and Tobler, J., p. 174 of ref. 1.

[67] Jungner, E. W., Ger. Pats. 199,250 (1908), 206,108 and 206,273 (1909).

[68] Baur, E., and Brunner, R., Z. Elektrochem., **43**, 725–7 (1937).

[69] Baur, E., and Preis, H., ibid., **43**, 727–32 (1937).

[70] Baur, E., and Preis, H., ibid., **44**, 695–8 (1938).

electrolytically conducting solid mixtures of 85 percent zirconium oxide and 15 percent yttrium oxide have been used heretofore in the Nernst lamp.[71] The properties of a large number of mixtures of this type have been studied by Baur, who recommended a composition of clay, rare-earth oxides from the ignition of monazite sand, and tungsten trioxide. The resistance of small tubes of 1-millimeter wall thickness

difficulties. Commercial solid fuels cannot be employed because of accumulation of ash, and hence expensive gaseous fuels are required. Also, the tubes of solid electrolyte would appear to be both expensive and fragile. The high operating temperature of 1,100° C would entail large heat losses as well as difficult maintenance. From the original cell, the output was estimated to be 10 watts per liter of vol-
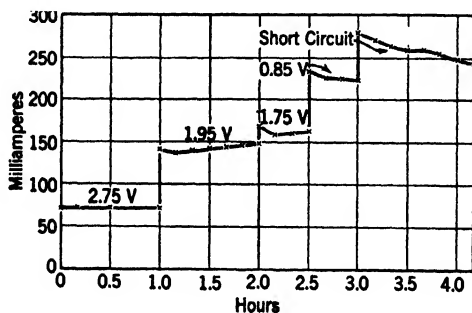
Fig. 5.   Characteristics of solid-electrolyte cell under load.[69]

formed from this composition was said to be 2 ohms per 20 square centimeters of conducting area at 1,100° C. A cell using such a solid electrolyte is shown in Fig. 4. Measurements on five such cells in series showed an open-circuit voltage of 0.7 volt per cell compared with the theoretical value of 1.0. The behavior under load is illustrated by the curve of Fig. 5, where current is plotted as a function of time and the terminal voltage of the five cells in series is indicated for each load. Baur[72] claimed that the cell is free from polarization almost to short circuit and that the cell at any given load quickly assumes a steady state.

Although Baur's cells with a solid electrolyte represent an interesting theoretical advance, there are many obvious practical

ume.[69] A larger cell, however, showed only 0.6 to 0.77 watt per liter.[70]

CELLS OPERATING ON DISSOLVED REACTION PRODUCTS

In cells of this type the chemical reducing action may take place either in the anode compartment of the cell or in a separate operation. In either event the electrical energy is produced by electrical oxidation of the reduction product. It has often been proposed to use salts of metals of variable valence which are alternately reduced chemically by carbon or a reducing gas and oxidized in the cell to furnish electrical energy. Examples of such cells are those oxidizing sulfurous to sulfuric acid,[73, 74] hydrogen iodide to iodine,[75] cu-

71 Nernst, W., ibid., 6, 41–3 (1899).
72 See p. 698 of ref. 70.

73 Jungner, E. W., Ger. Pat. 199,250 (1908).
74 Taitelbaum, I., Z. Elektrochem., 16, 290–300 (1910). Baur, E., ibid., 16, 300–302 (1910).

prous to cupric salts,[76] cerous to ceric salts,[77] ferrous to ferric salts,[78] and those employing thallium and vanadium compounds,[79] titanium, thallium, and cerium compounds.[80] Glasses containing variable-valence metallic oxides, such as those of manganese, uranium, vanadium, cerium, and chromium, have also been investigated.[81]

Though all these cells have eliminated, to a certain degree, the problem of the sluggish kinetic behavior of carbon or the reducing gases produced therefrom, none has a sufficiently high reaction rate to permit the withdrawal of energy at commercially significant current densities, and, furthermore, in many cases the higher reaction rate has been obtained only at the expense of a large fraction of the free energy change available in the oxidation of carbon.

CELLS OPERATING ON SOLID REACTION PRODUCTS OF CARBON

It was proposed very early, in order to avoid the problems in connection with carbon or gas electrodes, that readily ionizable metal electrodes be prepared by chemical reduction with carbon and that the oxidized metal compound from the cell reaction be again reduced to the metallic form, and so forth. Faure[82] proposed such a cell using an iron anode and aqueous sodium chloride electrolyte. After the cell reaction had taken place the iron was precipitated as carbonate, separated by filtration, and

reduced again to metallic iron. Analogous reaction schemes have been proposed for lead, tin, cadmium, and antimony.[83] Subsequently Rideal and Evans[84] studied similar cells using lead anodes in an alkaline electrolyte and tin in an acid one, better results being obtained with the second. Reed,[85] in his excellent critical analysis of the problem, pointed out the low efficiency, about 2 percent, to be expected from such a cell burning zinc as a fuel. Cells using sodium as the "fuel" electrode have also been described.[86] In a cell operating on iron, the reduction of ferric iron to the metallic state will require 77 grams of coal per gram atom of iron, if the reduction is carried out in a blast furnace,[87] and this gram atom of iron will furnish 0.1 kilowatt-hour if oxidized to ferric oxide at 100 percent efficiency in an iron-oxygen cell[88] operating at 25° C, but this same weight of coal would produce 0.12 kilowatt-hour in a high-pressure steam plant.[32] Not only do many examples of this type of fuel cell suffer from large free energy losses, in preparation of the "fuel," but also the actual cost of the reduction process itself may be considerable.

AIR ELECTRODES

For the operation of a fuel cell the cathode reactions are of equal importance to those taking place at the anode, and, although some of the cathode reactions have been discussed in earlier paragraphs, in connection with reactions of the complete

[75] Siemens-Schuckertwerke, Ger. Pat. 284,821 (1915).

[76] Tatlow, W., *Electrician*, **34**, 344 (1894–5).

[77] Welsbach, Auer von, *Chem. Z.*, **1**, 690 (1902). Baur, E., and Glaessner, A., *Z. Elektrochem.*, **9**, 534–9 (1903).

[78] Keÿzer, H. J., Brit. Pat. 3,913 (1904).

[79] See pp. 294–5 of ref. 17.

[80] Nernst, W., Ger. Pats. 264,026, and 265,424 (1913).

[81] See p. 476 of ref. 41.

[82] Faure, C. A., Ger. Pat. 57,316 (1891).

[83] Jone, H., U. S. Pat. 764,595 (1904).

[84] See p. 479 of ref. 41.

[85] See pp. 74–5 of ref. 15.

[86] Habicht, F. P., Brit. Pat. 143,532 (1920). Baur, E., *Z. Elektrochem.*, **27**, 194–9 (1921). Brandt, R., Ger. Pat. 408,435 (1925).

[87] Shore, F. M., and Bennit, H. L., *Minerals Yearbook, Review of 1937*, U. S. Bur. Mines, p. 788 (1938).

[88] Chipman, J., and Murphy, D. W., *Ind. Eng. Chem.*, **25**, 319–27 (1933).

cells, this phase of the problem is of sufficient importance to merit further emphasis. The ideal cathode would be an electrode showing the theoretical potential of the oxygen electrode at an oxygen partial pressure corresponding to the oxygen content of the air and functioning at a sufficiently high rate to permit the flow of useful amounts of current with relatively small polarization effects. The difficulties in the way of the attainment of this ideal cathode have been as great as or greater than those already discussed in connection with the anodic functioning of carbon or its reaction products. It has been stated [89] that "the achievement of a fuel cell · · · has encountered its most serious difficulties at the oxygen electrode. Gaseous oxygen establishes its potential sluggishly and imperfectly on inert electrodes at ordinary temperatures, even on open circuit, and an oxygen electrode on closed circuit polarizes at once if any appreciable current is withdrawn." There is, however, some evidence that progress is being made. The investigations in this field can be conveniently classified according to the type of electrode into: (a) noble metal, (b) base metal or oxide, (c) special carbon.

In many instances the overall reaction rate may be increased by surrounding the cathode with a solution of an oxidizing agent prepared either directly in the cell or in a reaction outside of it. In analogy with the use of solutions of reducing agents at the anode, such oxidizing agents employed at the cathode should exhibit a potential near that of the theoretical air electrode or the efficiency of the cell will suffer.

NOBLE-METAL CATHODES

The electromotive behavior of oxygen at the surface of a noble metal is even less satisfactory than that of hydrogen or carbon monoxide. It is more difficult to reach the theoretical potentials, and those attained are less stable. Baur [90] pointed out that the fatigue phenomena of oxygen electrodes of platinum militate more against their technical application than does cost.

Many workers have used simple platinum cathodes; [16, 18, 21, 28, 30, 34, 36, 37, 38, 39,-40, 57, 91] others, platinum upon a special support such as clay [42] or porous carbon. [45, 46, 91]   Palladium [30, 45, 64] and gold [24, 30] have been less extensively employed. With few exceptions, experimenters have made no attempt to determine the behavior of the cathode independently from that of the anode, so that no conclusions can be drawn, in most cases, as to the exact performance of the air electrodes. Naray-Szabo [91] studied the cathodic behavior of platinized porous carbon "diffusion electrodes" of the type used by Schmid [44] for hydrogen electrodes. The air electrode was combined with a large zinc anode in acid and alkaline electrolytes. This investigator has concluded that such electrodes are useful up to current densities of 4 to 5 amperes per square decimeter. Data given, however, show that the potential of this air electrode fell from an open-circuit value of 0.963 volt to 0.0751 volt at a current density of 1.0 ampere per square decimeter. These data were obtained in $2 N$ sulfuric acid at room temperature. Fifteen percent sodium hydroxide and 27 percent ammonium chloride gave even less favorable results.

BASE-METAL CATHODES

Many workers have used cathodes of iron [12, 16, 18, 20, 23, 26, 28, 53, 59] and of nick-

[89] Lamb, A. B., and Elder, R. W., J. Am. Chem. Soc., 53, 137–63 (1931).

[90] Baur, E., and Tobler, J., p. 177 of ref. 1.
[91] Naray-Szabo, Stefan v., Z. Elektrochem., 33, 15–20 (1927).

el [23, 28, 61, 92] or their oxides, especially at elevated temperatures. Silver cathodes were first used at normal temperatures [18, 52] in cells with aqueous electrolytes and later [19, 23, 26, 47] at elevated temperatures with fused electrolytes. Copper or copper oxide cathodes have been used [9, 28, 30, 47, 51, 55] over a wide temperature range. The results of Baur and Ehrenberg [19] with the molten silver cathode and of Baur, Treadwell, and Trümpler [26] with magnetite cathodes have been outstanding. Baur, Petersen, and Füllemann [23] measured the potentials of cells composed of various metal oxides and showed that these are in the same order as the equilibrium oxygen partial pressures of the oxides.

Antimony [52] and mercuric oxides [83] were used in two early cells. Baur [93] studied the action of a mixed oxide depolarizer, "Hopcalite," in a dry cell. It showed somewhat lower initial potentials but maintained the potential better under load.

CARBON CATHODES

Many of the earlier cells operating both with aqueous electrolytes and with fused salts at elevated temperatures employed carbon cathodes.[7, 9, 11, 49, 52, 73] It is only comparatively recently, however, that the specific activating properties of carbon surfaces for oxygen have been recognized. Although such electrodes do not at present give promise of sufficiently high reaction rates to function as cathodes in a "fuel cell," they have already found application for cells of limited current demands.

Fery's cell [94] depends upon the activating properties of a special porous-carbon cathode for depolarization. In this cell,

the manganese dioxide is dispensed with and depolarization is effected by oxygen from the air, activated at the surface of a large porous-carbon electrode. The capacity of cells with air depolarization is stated to be approximately 20 ampere-hours per pound, the electromotive force on open circuit, 1.18 volts.

Nasarischwily [95] made a study of air depolarization and found that the maximum current which could be drawn without excessive polarization was approximately 0.03 ampere per square decimeter of superficial carbon area.

Heise and Schumacher [96] have described an air depolarized cell for commercial use. The air electrode is said to be nongraphitic carbon with powdered charcoal as one of the principal constituents. It must be sufficiently porous to permit adequate access of air, and yet the pore size must be small enough to offer resistance to electrolyte penetration. Normal reaction rates of 0.5 ampere per square decimeter may be maintained merely by contact with the air. By forcing air through the electrode the rate may be increased many fold. The absorption is about theoretical, 0.3 gram of oxygen per ampere-hour under normal operating conditions. Because of adsorbed oxygen, the electrode continues to function for some time after the air supply is interrupted. It is essential that the electrode remain substantially dry, except at the electrode-electrolyte interface, and this is accomplished by controlled impregnation with paraffin. The potential of the carbon cathode is normally a few tenths of a volt below that of a reversible oxygen electrode and hence, like that of the platinum black-

[92] Gore, G., *Phil. Mag.*, **27**, 446–51 (1864).

[93] Baur, E., *Z. Elektrochem.*, **36**, 410–4 (1930).

[94] Fery, C., *La Nature*, **90**, 224 (1918); also described in a news item in *Ind. Eng. Chem.*, **10**, 744 (1918).

[95] Nasarischwily, A., *Z. Elektrochem.*, **29**, 320–3 (1923).

[96] Heise, G. W., and Schumacher, E. A., *Trans. Electrochem. Soc.*, **62**, 383–91 (1932).

oxygen electrode, may be considered as due to oxide complexes which serve as the depolarizer.

REACTION PRODUCTS OF OXYGEN

Some of these oxidizing agents can be prepared simply by the direct action of oxygen, but others would have to be made in a complicated series of reactions outside of the cell and hence represent a very expensive form of oxidant for reaction with the "fuel."

Halogens such as chlorine and bromine represent a satisfactory type of cathodic depolarizer and have been used by many workers. Schmid [44] has shown, for example, that chlorine is readily activated at carbon surfaces. It has been proposed [97] to prepare the chlorine by the action of air on chlorides in the presence of copper salts, the Deacon process. The chlorides would be recovered from the cell so that the process, theoretically, would be cyclical. Such a cycle would be too expensive to have any bearing on the fuel-cell problem.

Several cells operating with fused electrolytes [16, 17, 24, 41] have used compounds of variable-valence amphoteric elements such as manganese, and many of the early cells probably depended partly on the presence of manganates as an impurity in the fused alkali.

Winand,[48] Borchers,[49] and Lamb and Elder [89] used copper salts either alone or in admixture with oxidizing agents.

Ferric salts have been used by Zettel [98] and by Lamb and Elder.[89]

Case [99] used potassium chlorate; Hofmann and Ritter,[21] sodium hypochlorite; and Siemans-Schuckert,[75] nitric acid.

Lamb and Elder [89] pointed out that there

are combinations such as the thallous-thallic and vanadyl-vanadic which give potentials close to the value for the oxygen electrode but react with oxygen too slowly to be of value; other combinations such as the vanadous-vanadic and the chromous-chromic react rapidly with oxygen but furnish too low a potential. They stated that the ferrous-ferric system appears to be one of the most favorable, yielding a fairly high potential and reacting at a measurable rate with oxygen. These workers made a detailed study of the kinetics of the oxidation of ferrous salts with oxygen. Agitation, the addition of copper salts, platinum black, and activated carbon were all found to have a beneficial effect on the rate. Solutions of ferrous salts containing pyrophosphate were found to oxidize 1,000 fold faster but showed a much lower potential. Direct measurements in a cell of the depolarizing activity of ferrous sulfate solutions containing copper salts and activated carbon showed that higher current densities could be employed with less polarization than with any other oxygen electrode operating at room temperatures which has yet been described. The potential decreased only from an open-circuit value of 0.659 to 0.606 volt at 2.15 amperes per square decimeter. Such an electrode, if combined with a hydrogen electrode, would furnish, it was estimated, 0.94 kilowatt per cubic meter of electrolyte.

ECONOMICS

With few exceptions the cells which have been described in the previous pages have operated on special and expensive types of fuels, and, as has been pointed out in several instances, the added cost of the raw material for the production of the energy more than compensates for any possible advantages due to the increased efficiency

[97] Nernst, W., Ger. Pat. 259,241 (1913). For a brief discussion see p. 180 of ref. 1.

[98] Zettel, T., Z. Elektrochem., 2, 543–5 (1896).

[99] Case, W. E., see p. 170 of ref. 1.

of the process. A power plant burning a 13,000-Btu coal costing $3.00 per ton is obtaining its raw material for electrical energy at 0.04 cent per kilowatt-hour. Hydrogen at 3.2 cents per 1,000 cubic feet, carbon monoxide at 3.8 cents, methane at 10.6 cents, and coke-oven gas at 7 cents would be comparable fuels.[100] If the fuel cell can be made to operate at two to three times the efficiency of the thermal-mechanical cycle, such a plant could afford to pay, for a gaseous fuel, two to threefold the above prices, other cost items being equal.

No cell has yet been operated, even in the laboratory, on the lowest-cost fuel, bituminous coal. There are numerous obvious difficulties. Coal, when acting as a reducing agent at temperatures below 100° C, is oxidized incompletely with the formation of a whole series of complex organic acids such as humic acids and those of the benzene carboxylic series (see Chapter 9). Some of this last group are especially difficult to oxidize further, so that the full amount of energy corresponding to complete oxidation of the coal to carbon dioxide and water cannot be obtained. Operations at temperatures higher than 100° C necessitate either the use of a pressure cell or an electrolyte having a low vapor pressure at elevated temperatures, such as a fused salt. The use of coal as a reducing agent at temperatures above 350 to 400° C would be complicated by thermal decomposition of the fuel and the liberation of gases and tars in the cell. Finally, all coals contain inorganic constituents, the ash, in greater or less amounts, and this

material would accumulate in the electrolyte and require its periodic purification or replacement.

The use of coke in a fuel cell would eliminate some of the difficulties pointed out above in connection with coal but would be less desirable in several other ways; the original cost of the energy would be 50 to 100 percent higher; coke has a lower reactivity, and hence the cell would have to operate at a higher temperature and the ash problem would be aggravated since the ash content of coke is necessarily higher than that of the coal from which it is prepared.

By the use of gaseous fuels in a cell many of the objections raised in connection with the solid fuels would be eliminated. They are free from ash, and gases such as hydrogen and carbon monoxide are effective reducing agents at moderate temperatures. Methane is much less reactive, of course, and would require operation of the cell at elevated temperatures. There remains for all these gaseous fuels the inherent difficulty of high cost per unit of energy. Conceivably, however, there are certain applications where, if gaseous fuels were cheaply available and there were a demand for low-voltage direct current, a fuel cell could be economically justified. The plant would consist of a large number of comparatively small units of small energy output per unit of volume and probably high capital and maintenance costs. Since the only cells in which the technical problems have been even partially solved are those employing gaseous fuels, it is evident that large-scale application of the fuel cell is extremely doubtful until the cost of energy in the form of such gaseous fuels has been significantly reduced.

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[100] Calculated at 1 atmosphere and 15.5° C (60° F). Coke-oven gas is assumed to be 600 Btu.

PRODUCERS AND PRODUCER GAS

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The producer process is a method for complete gasification of solid fuels. In the producer process the fuel is primarily heated up by the hot gases made, thereby losing its volatile matter. The coke residue remaining after this carbonization process is gasified by conversion to products of incomplete combustion, principally carbon monoxide.

The producer process is a continuous one. The nature of the gas made is subject to considerable variation, depending on the type of producer. Whereas in former years producer gas meant a fuel gas of relatively low heating value, 110 to 160 Btu per cubic foot, the technique of making it has been changed with the use of oxygen instead of air blast to give a gas of heating value approaching that of coal-distillation gases, 400 to 500 Btu per cubic foot. Such gases are no longer devoted exclusively to heating purposes but serve a useful role in chemical synthesis. Owing to economic conditions, most of these developments have taken place abroad rather than in the United States.

The price of fuel is the principal item in the cost of making of ordinary producer gas, and as a result producers are principally used for gasification of the cheaper solid fuels. The popularity of producers has decreased since about 1930 with the development of efficient stokers for cheap fuels. Furthermore, producer gas as an intermediary in converting solid fuels to power directly by means of combustion engines has almost become obsolete in the United States with the development of small Diesel engine units and cheap hydroelectric power. Increased utilization of blast-furnace gas and coke-oven gas for heating purposes in steel mills has greatly contributed to the decreased use of producers.

There has taken place abroad a revival of the producer-type process for two purposes: one, as previously mentioned, serves to manufacture special gases from cheap solid fuels; and the other, to supply power for automotive engines. Even though these two processes do not seem directly applicable to the United States because of economic reasons their development has shown that the producer process has great flexibility and their study stimulates thought of new applications. A great deal of chemical as well as mechanical ingenuity has been exhibited in some of this work; the capacity of gas production has been raised to values many times those of the well-established older types of apparatus.

The mechanical coal, or coke, producer was developed in the United States to a considerable degree of perfection and the capacity raised to a figure unheard of in the days of stationary, hand-fed machines.

Dickerman [1] of the Federal Trade Commission has stated in 1936 that there were installed about 3,800 mechanical and about 1,000 hand-fed producers in the United States, about 2,000 mechanical and 600 hand-fed machines being in continuous or periodic use. Whereas the mechanical producers gasified on the average 2,000 pounds of coal per hour, making 65 cubic feet of gas of 148 Btu per cubic foot per pound of coal, the hand-fed machines gasified only 600 pounds of coal per hour to give 65 cubic feet of 140 Btu gas per pound of coal.

The maximum capacity of a conventional mechanical coal producer is somewhere near 8,000 pounds of coal per hour, or about 100 pounds per hour per square foot cross-sectional area. For comparison, a modern Winkler producer will gasify as much as 62,000 pounds of dry lignite per hour, or approximately 480 pounds per hour per square foot, and a throughput of as high as 700 pounds per hour per square foot is claimed in the Philipon slagging producer. The Winkler producer is capable furthermore of making a gas with a heating value very close to 300 Btu per cubic foot. Such developments cannot be ignored.

On the theoretical side there seem to be signs of a somewhat revolutionary change in conception of the fundamental processes going on inside a producer. Conventional theory holds that carbon dioxide is primarily formed from the carbonaceous fuel and carbon monoxide is subsequently produced by a reduction process. Newer theories claim that carbon monoxide appears as a primary product of incomplete combustion and furnish an explanation of the possibility of attaining extremely fast operating rates.

[1] Dickerman, J. C., *Trans. World Power Conf.*, *3rd Conf. Washington, 1936*, **4**, 491–542 (1938).

FUNDAMENTAL GAS REACTIONS

THERMODYNAMIC DATA

The set of eight gas reactions listed in Table I is fundamental in the study of the combustion of carbonaceous solid fuels as well as of the conversion of such fuels into gaseous fuel. The principal thermodynamic constants, molar change in enthalpy ($\Delta H°$) and in free energy ($\Delta F°$), of the reactions are included in Table I. The values given for $\Delta H°$ and $\Delta F°$ are taken from the *International Critical Tables* [2] and are expressed in gram calories per gram mole. A negative $\Delta H°$ value indicates a positive heat of reaction, and a negative $\Delta F°$ value results in a positive value for the expression,

TABLE I

THERMODYNAMIC CONSTANTS OF FUNDAMENTAL GAS REACTIONS

No.	Reaction	$\Delta H°_{291°K}$	$\Delta F°_{298.1°K}$
1	$C_{gr} + (O_2)_g = (CO_2)_g$	−94,390	−94,260
2	$C_{gr} + \frac{1}{2}(O_2)_g = CO_g$	−26,490	−32,510
3	$C_{gr} + (CO_2)_g = 2CO_g$	+41,410	+29,240
4	$CO_g + \frac{1}{2}(O_2)_g = (CO_2)_g$	−67,900	−61,750
5	$(H_2)_g + \frac{1}{2}(O_2)_g = H_2O_g$	−57,830	−54,507
6	$C_{gr} + H_2O_g = CO_g + (H_2)_g$	+31,340	+22,000
7	$C_{gr} + 2H_2O_g = (CO_2)_g + 2(H_2)_g$	+21,270	+14,760
8	$(CO_2)_g + (H_2)_g = CO_g + H_2O_g$	+10,070	+7,240

$RT \ln K_p$, K_p being the reaction constant at constant pressure, computed in the customary manner.

The standard state for carbon is graphite, its high-temperature form, while the standard state for the gaseous compounds is defined by the standard temperature indicated in degrees Kelvin and by atmospheric pressure. Reactions 1, 4, and 5 are the fundamental ones for calorimetric $\Delta H°$ determinations, and all others can be found therefrom. Reactions 3, 4, 5, and 8 are the fundamental ones for $\Delta F°$ determinations by equilibrium studies, and the others

[2] *International Critical Tables*, National Research Council, McGraw-Hill Book Co., New York, 1929, **5**, 176, 181–2, **7**, 231–2, 243–4.

are derived from them. For conversion to Btu per pound mole, the H or F values should be multiplied by a factor 1.800.

Later values of constants of the fundamental reactions have been given by sev-

ture, standard reference books on physical chemistry should be consulted.[4]

Since all these reactions are reversible, information regarding the equilibrium constant K_p and its change with temperature
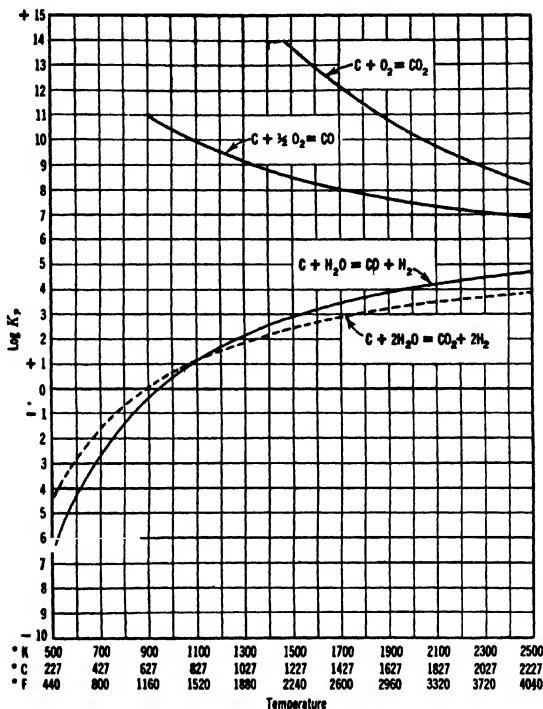
FIG. 1. Variation of log K_p with temperature for reactions 1, 2, 6, and 7.

eral authors.[3] The accuracy of the principal values is 1 percent or better. For further data regarding these reactions and the changes of ΔH and ΔF with tempera-

is of interest. Figures 1 and 2 show the relations between log K_p and T. All data thus obtained are those of equilibrium mixtures, and, more often than not, these values are not attained in actual gases at the temperatures used in practice. The

[3] Rossini, F. D., J. Research Natl. Bur. Standards, 6, 1–35, 37–49 (1931), 22, 407–14 (1939) ; J. Chem. Phys., 6, 569 (1938). Bryant, W. M. D., Ind. Eng. Chem., 23, 1019–24 (1931). Kassel, L. S., J. Am. Chem. Soc., 56, 1838–42 (1934). Terebesi, L., Helv. Chim. Acta, 17, 819–37 (1934). Meyer, G., and Scheffer, F. E. C., Rec. trav. chim., 57, 604–8 (1938).

[4] Lewis, G. N., and Randall, M., Thermodynamics, McGraw-Hill Book Co., New York, 1923, 653 pp. Taylor, H. S., A Treatise on Physical Chemistry, D. Van Nostrand Co., New York, 1925, 2 vols., 1823 pp.

rate of approach of the reactions to equilibrium is the subject of the study of their kinetics and can be influenced by various factors such as surface effects and catalysts. Since the equilibrium constants of reactions 3, 6, 7, and 8 are measurable in the tem-

These reactions, which are among the most common ones in physical chemistry, have been studied nearly incessantly. Since they represent the process of carbon combustion, study of their mechanism is of great importance. (See also Chapters 24
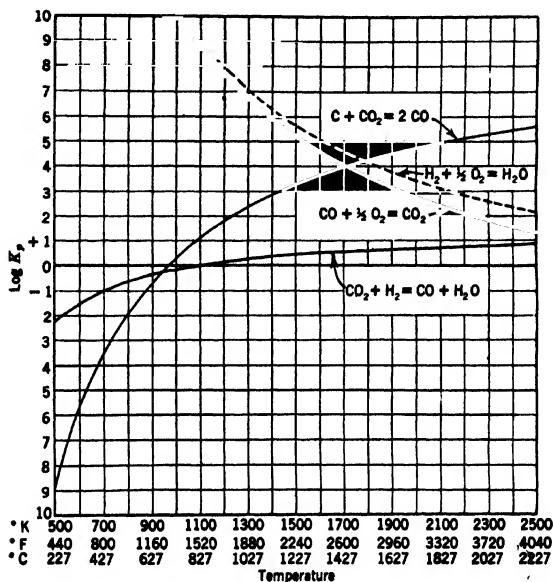
FIG. 2. Variation of log K_p with temperature for reactions 3, 4, 5, and 8.

perature range of common producer practice, these equilibria are of primary significance for the present study. In most equilibria determinations graphite is assumed to be the form of carbon present at the high temperatures usually employed. With other forms of carbon, equilibria might conceivably be shifted slightly, but such influence is more likely to affect reaction rates rather than final equilibria.

and 33.) In 1913 Rhead and Wheeler [5] assumed that in the reaction of carbon with oxygen neither reaction 1 nor 2 actually took place but that an intermediary solid product C_xO_y was first formed and subsequently decomposed to a mixture of carbon monoxide and carbon dioxide. The ratio of monoxide to dioxide in the evolved mixture depended on temperature. Several other authors [6] have pursued the study of the

KINETIC DATA

(1) $$C + O_2 = CO_2$$

(2) $$C + \tfrac{1}{2}O_2 = CO$$

[5] Rhead, T. F. E., and Wheeler, R. V., *J. Chem. Soc.*, **101**, 846–56 (1912), **103**, 461–89 (1913).

[6] Langmuir, I., *J. Am. Chem. Soc.*, **37**, 1139–67 (1915). Sihvonen, V., *Z. Elektrochem.*, **36**,

mechanism of carbon combustion and of the structure of the possible intermediary solid compounds of oxygen and graphite often at low pressures to prevent secondary reactions. An able review of the organo-chemical work in the theory of combustion of carbon was given by Riley [7] and later by Strickland-Constable,[8] as well as by Bang-ham and Bennett [9] and Lambert.[10] This work leaves wide open the question whether the monoxide or the dioxide is the primary product of carbon combustion. Determinations of useful reaction rates are not included in any of this work.

Burke and Schumann [11] worked out an interesting theory of combustion of carbon in which it was assumed that, in an at-mosphere containing oxygen, the carbon particles surround themselves with a film of high carbon dioxide concentration, the carbon dioxide diffusing outwardly against the incoming oxygen and also inwardly to-wards the carbon, being there reduced to the monoxide. The overall result is the reaction on the carbon surface of $C + CO_2 = 2CO$, in the surrounding film of $2CO + O_2 = 2CO_2$. Experiments by Du-binsky [12] and by Mayers [13] seem to contra-dict Burke's hypothesis.

Outstanding fundamental research on

carbon combustion has been done by Hot-tel and coworkers [14] following up earlier investigations of Smith and Gudmundsen.[15] Graphite spheres of 1-inch diameter were burnt in oxygen, carbon dioxide, or steam atmospheres at temperatures up to 1,350° C, using gas velocities ranging from 3.5 to 50 centimeters per second (0.1 to 1.6 feet per second). Their curves of log K, the reac-tion constant, versus T, temperature, at different gas velocities had two distinct trends. At low temperatures the rise was steep, indicating that chemical resistance controlled the reaction rate; at high tem-peratures the diffusion of gas to and from the carbon surface controlled the rate and thus the rate depended less on temperature and more on gas velocity. The tempera-ture at which the curves changed lay be-tween 1,000 and 1,100° K (1,340 and 1,520° F). The increase in reaction rate with temperature below 1,000° K followed fairly well from values of activation heat A, calculated from the Arrhenius equation, of 20,000 to 30,000 calories per mole of oxygen, such as determined by Meyer.[16] In the range controlled by chemical resist-ance the combustion rate doubled for every 15° C at 1,050° K; in the range controlled by diffusion the rate varied as the 0.6 to 1.1 power of the absolute temperature and as the 0 4 to 0 7 power of the mass velocity. In the diffusion-controlled ranges, it was assumed that carbon dioxide was formed at the carbon surface, diffusing through the inert nitrogen layer outward from the car-bon and the oxygen diffusing in the reverse direction toward the carbon surface.

806–7 (1930), **40**, 456–60 (1934) ; *Trans. Fara-day Soc*, **34**, 1002 (1938). Boersch, H, and Meyer, L., *Z. physik. Chem.*, **B29**, 59–64 (1935) ; *Trans. Faraday Soc.*, **34**, 1056 (1938).
    7 Riley, H. L., *J. Inst. Fuel*, **10**, 149–56 (1937).
    8 Strickland-Constable, R. F., *Fuel*, **19**, 89–93 (1940).
    9 Bangham, D. H., and Bennett, J G, *ibid*, **19**, 95–101 (1940).
    10 Lambert, J. D., *Trans. Faraday Soc.*, **32**, 452–62, 1584–91 (1936).
    11 Burke, S. P., and Schumann, T. E. W., *Ind. Eng Chem.*, **23**, 406–13 (1931) ; *Proc. 3rd In-tern. Conf. Bituminous Coal*, **2**, 485–509 (1931).
    12 Dubinsky, S. M., M. S. thesis, Mass. Inst. Technology, 1932.
    13 Mayers, M. A., *J. Am. Chem. Soc.*, **56**, 70–6 (1934).

    14 Tu, C. M., Davis, H., and Hottel, H. C., *Ind Eng Chem*, **26**, 749–56 (1934). Davis, H, and Hottel, H. C., *ibid.*, **26**, 889–92 (1934). Parker, A. S, and Hottel, H. C., *ibid.*, **28**, 1334–41 (1936).
    15 Smith, D. F., and Gudmundsen, A., *ibid*, **23**, 277–85 (1931).
    16 Meyer, L., *Z. physik. Chem.*, **B17**, 385–404 (1932) ; *Z. Elektrochem.*, **9**, 640–1 (1934).

Later experiments published in 1936 with somewhat higher gas velocities showed for the combustion of carbon in air that the percentage of oxygen at the carbon surface ($\frac{1}{2}$ millimeter distance) dropped from 20 percent at 1,000° K to 2 percent at 1,350° K for 150 centimeters per second (5 feet per second) air velocity of approach and from 17 to 0.6 percent for 3 centimeters per second (0.1 foot per second) air velocity of approach. The reaction rate 10^3K (grams carbon per square centimeter carbon surface per second) tapered off to 0.5 for 150 centimeters per second velocity and to 0.12 for 3 centimeters per second velocity at temperatures above 1,500° (Fig. 3). Little carbon monoxide was formed at the surface, and K was proportional to the 0.37 power of mass velocity. The value for activation heat derived from the later experiments was 44,000 calories.

In all Hottel's work, brush carbon (graphite) was used having 0.17 percent by weight of ash. A complete equation was given by Hottel and Parker expressing the rate of reaction in known physical factors and certain constants and covering both ranges of combustion.

The studies of the authors so far mentioned have been concerned principally with the mechanism and the rate of the reaction of carbon with oxygen, carried out on a model scale in order to simplify the assumptions for the calculation of the experimental results. The greater part of the work on the combustion of carbon has been carried out in somewhat different manner, viz., by passing an air current through a bed of fuel consisting of irregular particles of different nature and size, such as pulverized coke. If such tests are conducted with fuel beds only a few inches thick, the results are especially significant for combustion-rate determinations; if the fuel beds are thicker, of the order of 6 to 24 inches, results are significant for producer reaction determinations. Tests of this type are also generally employed for the determination of the factor of "reactivity" of the fuel, and this factor influences the combustion and producer reactions.

Reaction rates, the mathematics and physics of combustion in fuel-beds, the de-
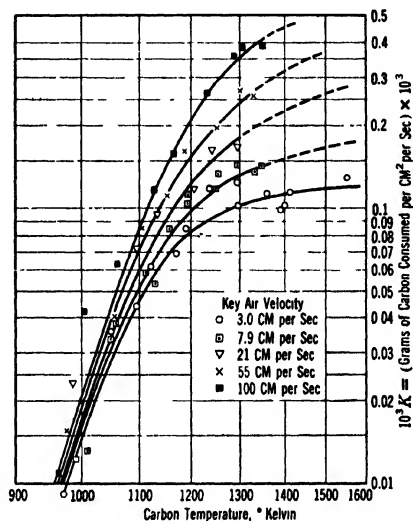
FIG. 3   Effect of temperature and ambient air velocity on combustion rate. After Parker and Hottel.[14]

termination of ignition temperatures, etc., are dealt with in a number of papers by Mayers and coworkers.[17]

Using different samples of 40- to 60-mesh pulverized coke in a 1-inch layer, with an air velocity about 1 inch per second, Sebastian and Mayers[17] determined the constants b' and E in the equation for the reaction rate μ:.

17 Mayers, M. A., *Chem. Revs.*, **14**, 31–53 (1934) ; *Trans. Am. Inst. Mining Met. Engrs.*, **130**, 408 23 (1938). Sebastian, J. J. S., and Mayers, M. A., *Ind. Eng. Chem.*, **29**, 1118–24 (1937). Mayers, M. A., and Landau, H. G., *ibid.*, **32**, 563–8 (1940).

$$\log_e \mu = b' - \frac{E}{RT}$$

where μ is in milligrams of coke per gram per second per atmosphere. The ignition temperature was determined as the intersection of the coke temperature and the furnace temperature plotted versus time. At temperatures near the ignition point, the values for b' ranged from 6.0 to 20.4, and E (activation energy) from 11,000 to 39,000 calories. The reaction was found to be of the first order. The temperature range was extended to 550° C (1,020° F). Ignition temperatures determined for various samples of commercial coke ranged from 300° to 525° C; the reaction rates at 500° C ranged from 0.30 to 0.0077 milligram coke per gram per second. Near the ignition point, the more reactive coke samples obtained from low-temperature carbonization appeared to have a high reaction rate. With increasing temperature the reaction rate of the less reactive coke however increased more rapidly, and, as a result, the difference in reactivity of the various cokes disappeared to some extent at higher temperature and might even reverse itself. Generally both the b' and E values were smaller for the more reactive coke (7 and 13,000 respectively), and higher for the less reactive coke such as foundry coke (20 and 39,000 respectively).

Above 900° C the previously mentioned relation between the reaction rate and temperature no longer applies. In agreement with Hottel's findings chemical resistance then no longer controls the rate but instead the rate of diffusion of oxygen to the carbon surface becomes the controlling factor. The temperature coefficient at temperatures above 900° decreases, and the reaction rate can be expressed approximately in terms of G, the rate of gas flow through the fuel bed (pounds per square foot per hour), and the particle size. Mayers has given a value of the rate for the reaction

$$C + O_2 = CO_2 \text{ of } \mu_1 = 183G^{\frac{1}{3}}$$
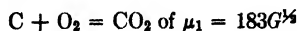
for underfeed stokers. This value agrees fairly well with Hottel's value of mass velocity to the 0.37 power as determined on single particles of graphite. For fairly large sizes of particles (of the order of 1 inch), μ_1 is inversely proportional to the average particle diameter.

Interesting light has been shed on the subject of combustion of carbon by two Russians, Grodzovskii and Chukhanov.[18] By blowing pulverized carbon particles in a vertical tube with a stream of air or oxygenated air from above, using a "fuel bed" of small height, combustion rates were determined. The air velocities were raised to a point well above that used previously by other authors. In the combustion tubes (3.2 up to 50 square centimeter cross section) velocities up to 10 meters per second (33 feet per second) were used. The reaction velocity was found to be very high; and, in no instance, regardless of rate or oxygen concentration, was any residual oxygen found. The combustion took place in a narrow zone (oxygen zone), the zone being thinner for higher velocities and for higher oxygen concentrations. With charcoal the oxygen zone decreased from 8.5 to 4 millimeters for velocities of 0.1 to 2.0 meters per second, and from 20 to 7 millimeters for air and 75 percent oxygen, respectively, with a velocity of 1.24 meters per second. On the basis of the gas analyses obtained, Grodzovskii and Chukhanov concluded that the formation of carbon monoxide is primary and explained thereby the very rapid combustion rates which never can be explained

[18] Grodzovskii, M. K., and Chukhanov, Z. F., *Fuel*, **15**, 321–8 (1936), **18**, 292 (1939).

from secondary monoxide formation by reduction of carbon dioxide. It was stated that at temperatures near the ignition point (600 to 700° C) the oxidation of C (charcoal) yields little monoxide, mostly dioxide. At temperatures above the ignition point, the monoxide formation increases and acquires a higher temperature coefficient with increasing temperatures. The mechanism was believed to be as follows:

At low velocities oxygen diffuses to the carbon surface, while monoxide diffuses away from the surface and encountering oxygen is converted partially or completely to the dioxide. For high blow velocities there is no longer sufficient time for the carbon monoxide combustion to take place, and all the primary monoxide is carried away from the surface and replaced by all the unconsumed oxygen. No limiting velocity for the combustion of carbon to the monoxide has been found. It is necessary to utilize compact fuel beds in order to attain the high gas velocities obtained in these tests. It would seem that the essential feature of this theory is the relatively slow rate of reaction 4 : $CO + \frac{1}{2}O_2 = CO_2$. Extreme rates were obtained by blasting a block of fuel with an atmosphere containing 90 percent by volume of oxygen at a velocity of 500 meters per second velocity. The gases formed under these conditions contained 85 percent of carbon monoxide and hydrogen.

Karzhavina [19] has published data substantiating the results of Grodzovskii. Wood charcoal, 2.5 to 5 millimeters in size, arranged in a 20-millimeter depth in a 40-millimeter reaction tube, was burned with a down blast of air or air-oxygen mixture. The gas produced was collected in 15 to 30 successive samples, corresponding to progressively thinner fuel beds. Channeling

[19] Karzhavina, N. A., *Fuel*, **19**, 220–5 (1940).

was prevented by continually leveling the top of the fuel bed, and the experiments were continued until the bed was a few millimeters thick.

The temperature of the burning layer increased with increasing air blast from 1,100° C to a maximum of 1,400° C at 0.80 meter per second blast velocity (in free space, standard conditions) and remained constant from there on up. The oxygen was consumed in a zone 7 to 15 millimeters thick, dependent slightly on either blast velocity (0.1 to 2.5 meters per second) or oxygen concentration (7 to 42 percent).

A distinct difference in gas composition was found with and without rapid chilling of the gas samples, this difference being wholly explainable by the combustion of carbon monoxide with excess oxygen after leaving the fuel bed. With rapid cooling, it was found that even in the initial few millimeters of the fuel bed carbon monoxide is formed. In the presence of 4 percent oxygen as much as 15 percent carbon monoxide was found with the straight air blast, and with the oxygen-enriched (42 percent) blast, 25 percent.

Factors contributing to high carbon dioxide formation were larger fuel size, larger free space between fuel particles, dilution of the fuel with Carborundum, and catalysis of carbon monoxide combustion by fuel ash. . It was concluded that the combustion of charcoal takes place as shown by the two following reactions (cf. Meyer, L., ref. 16):

(9) $4C + 3O_2 = 2CO_2 + 2CO$,

(10) $2C + O_2 = 2CO$
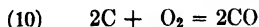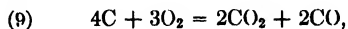
Reaction 9 is prevalent at low oxygen concentrations (5 percent or less) and takes place at low as well as high temperatures. Reaction 10 is usual at higher oxygen concentrations and above 800° C, the rate

being dependent upon the oxygen concentration. At blast rates above 0.3 meter per second, reaction 10 predominates and carbon dioxide is formed principally by secondary oxidation. The results obtained by Karzhavina are different in many respects from those obtained in experimental producers by Haslam and coworkers [20] and by Kreisinger.[21]

is given in Fig. 4. These curves are fundamentally different from the commonly accepted curves such as those discussed in a later chapter.

$$(6) \qquad C + H_2O = CO + H_2$$

$$(7) \qquad C + 2H_2O = CO_2 + 2H_2$$
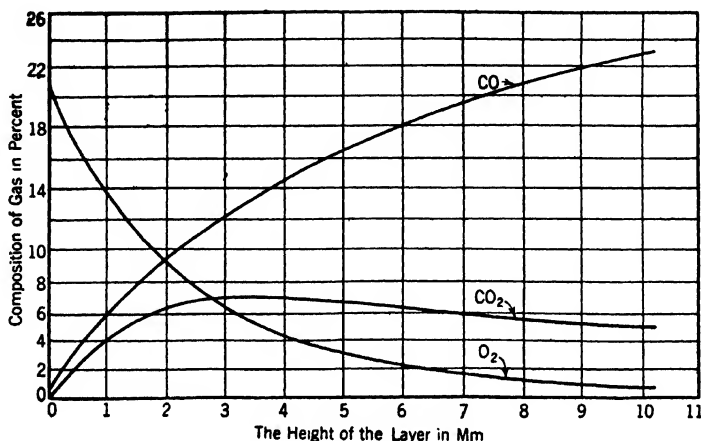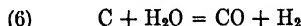
FIG. 4. Gas formation in a layer of wood charcoal.[19] Blast speed 0.81 meter per second, and analyses obtained on samples taken with a water-cooled sampler.

producers by Haslam and coworkers [20] and by Kreisinger.[21]

Further independent work on the mechanism of the reaction of carbon combustion appears necessary to settle the various controversial points. A typical set of curves illustrating the results of Karzhavina

Reactions 6 and 7 are essential to the process of water-gas manufacture and are of considerable importance in the producer process.

Studies of the organochemical mechanism of the reaction of $C + H_2O$ were made by Sihvonen [22] and others,[23] the primary effect being the formation of keto or diketo groups on the edges of the graphite crystals. The primary product given off is carbon monoxide, although at higher temperatures some keto groups may be oxidized with subsequent evolution of carbon diox-

20 Haslam, R. T., Ind. Eng. Chem., 16, 782–4 (1924). Haslam, R. T., Hitchcock, F. L., and Rudow, E. W., ibid., 15, 115 21 (1923). Haslam, R. T., Entwistle, F. E., and Gladding, W. E., ibid., 17, 586–8 (1925). Haslam, R. T., Mackie, R. F., and Reed, F. H., ibid., 19, 119–24 (1927). Haslam, R. T., Ward, J. T., and Mackie, R. F., ibid., 19, 141–4 (1927). Haslam, R. T., and Russell, R. P., Fuels and Their Combustion, McGraw-Hill Book Co., New York, 1926, 807 pp.

21 Kreisinger, H., Ovitz, F. K., and Augustine, C. E., U. S. Bur. Mines, Tech. Paper 137 (1917), 76 pp.

22 Sihvonen, V., Brennstoff-Chem., 17, 281–5 (1936); Trans. Faraday Soc., 34, 1062–74 (1938); Symposium on Solid Fuels, Am. Chem. Soc. Meeting, Boston, 1939, pp. 108–13.

23 Boersch, H., and Meyer, L., Trans. Faraday Soc., 34, 1056–61 (1938).

ide. The activation energy was reported as 90 large calories per mole, the reaction being of the zero order.

Mayers [24] determined the rate of attack of graphite by steam and concluded that reaction 6 takes place primarily, being followed by reaction 8 : $CO_2 + H_2$. At higher temperatures the monoxide to dioxide ratio was constant for different gas velocities; at lower temperatures the ratio increased with increasing velocity. (At 850° C this ratio ranged from 0.36 to 1.2 for throughputs of 11 and 30 liters per minute; at 980° C, from 0.1 to 1.3 for throughputs of 23 to 25.6 liters per minute; and at 1,050 and 1,150° C it was 0.30 for any throughput.) In the higher temperature range the reaction constant G_1 for reaction 6 was given by the expression

$$\log_{10} G_1 = 6.20 - \frac{35,130}{4.575T} \quad (1,000° - 1,160° \text{ C})$$

and at low temperatures by

$$\log_{10} G_1 = 8.42 - \frac{49,720}{4.575T} \quad (860° - 960° \text{ C})$$

In the above expressions, the units of G are micromoles per square centimeter per second. During the tests, the vapor pressure of water was maintained at 745 millimeters of mercury. It was remarked that the amount of hydrogen formed was always less in these reactions than that which corresponds to the oxygen in carbon monoxide and carbon dioxide. This was especially true at low temperatures. The discrepancy was attributed to methane formation.

For the investigation, short annular test pieces of graphite (21.3 millimeters diameter and 14 millimeters long) were utilized, of which only the outside polished cylindrical surface was exposed to the gases.

The tests were conducted at gas rates high enough to eliminate diffusion effects (5 to 35 liters per minute at standard conditions, linear velocity about 300 to 2,100 centimeters per minute). The apparent arbitrariness of having two equations for reaction rate was discussed at greater length in connection with the $C + CO_2$ reaction, which shows a similar discontinuity. Brief reference may be made here to similar work on controlled contact of steam with carbon described by Hottel and coworkers.

Besides determinations of reaction rates with pure graphite it is most important to determine reaction rates for water vapor and actual fuel beds. An elaborate critical review of the work of many authors on the water-gas reaction has been given by Dolch.[25] His conclusion was that only reaction 6 takes place and that subsequent carbon dioxide formation is the result of the gas reaction 8 : $CO + H_2O = H_2 + CO_2$. Results were cited of the work of Terres et al.,[26] who subjected several types of coke to the action of steam-nitrogen mixtures at temperatures between 400 and 1,200° C. For coke from coal, equilibrium was never reached in the contact times ranging from 200 to 10 seconds at temperatures below 1,200° C. The reactivity of the coke decreased with higher coking temperature. Other important work has been reported in papers by Bunte and others.[27]

Earlier work by Haslam and coworkers [28]

[24] Mayers, M. A., *J. Am. Chem. Soc.*, **56**, 1879–81 (1934).

[25] Dolch, P., *Wassergas*, J. A. Barth, Leipzig, 1936, 268 pp.

[26] Terres, E., Patscheke, G., et al., *Gas- u. Wasserfach*, **77**, 585–7, 628–36, 650–5, 666–9, 681–4, 703–6 (1934).

[27] Bunte, K., *Z. angew. Chem.*, **39**, 132–8 (1926). Bunte, K., and Giessen, A., *Gas- u. Wasserfach*, **73**, 241–7 (1930). Brender à Brandis, G. A., and LeNobel, J. W., *Het Gas*, **47**, 37–47 (1927). Dolch, M., and Kollwitz, F., *Braunkohle*, **30**, 445 (1931), **31**, 607–10, 628–32, 645–9 (1932).

[28] Haslam, R. T., Hitchcock, F. L., and Rudow, E. W., *Ind. Eng. Chem.*, **15**, 115–21 (1923).

on the reaction $H_2O + C$ (at temperatures 650° to 1,200°) led to a discussion of relative reaction rates somewhat different in its results from the opinions of Mayers, Terres, and Dolch. According to Haslam, reaction 7 plays an important role. Haslam's results are summarized in a square diagram giving hydrogen, carbon monoxide and carbon dioxide concentration as a function of the fraction of undecomposed steam shown in Fig. 5. The curves of this diagram are independent of the type of car-

bon, steam pressure, time of contact, or temperature.

It is generally accepted that the reaction rates ordinarily found in the contact of steam with carbonaceous fuel beds fall far short of attaining equilibrium for these reactions. One general conclusion may be drawn from the evidence on the $C + H_2O$ reaction, and that is, it does not reach equilibrium except at temperatures above 1,100° C (2,000° F). Expressing the progress of the reaction as the molar ratio
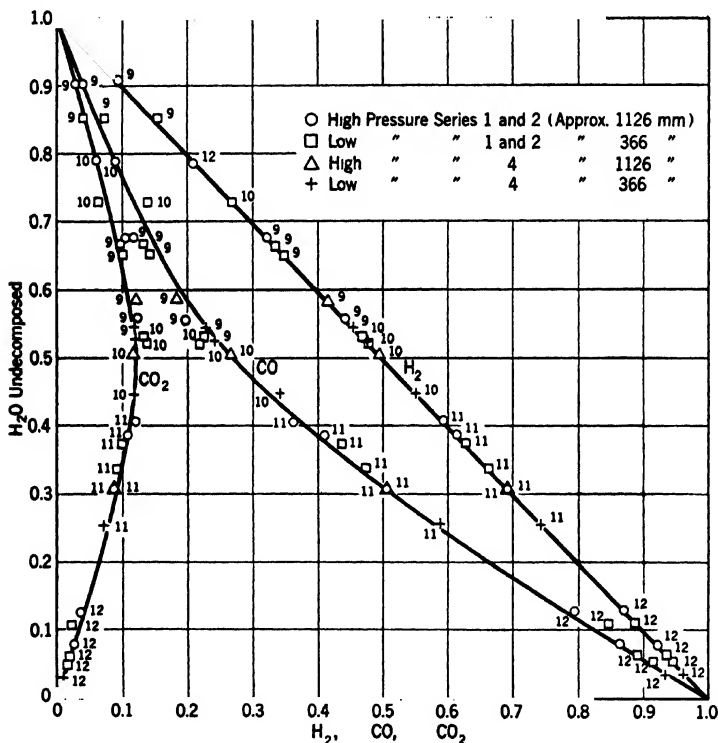
FIG. 5. Hydrogen, carbon monoxide, and carbon dioxide concentration as a function of undecomposed steam. The gas analyses correspond to the volumes of the constituents produced in the reaction $C + H_2O$ from a given unit volume of entering steam and are plotted against the fraction of undecomposed steam, $\dfrac{H_2O}{H_2O + H_2}$. The numerals are the temperatures of the reaction expressed in hundreds of Centigrade degrees.[18]

$H_2/(H_2 + H_2O)$ versus temperature, curve 1 of Fig. 6 shows the equilibrium ratios for the reaction $C + H_2O$ at different temperatures. Curves 2 and 3 are based on typical data of Terres [26] and of Cassan [29] respectively, for furnace coke, and curve 4 represents data obtained by Cassan [29] for graphite. Cassan's curves actually represent his "reactivity" value of "actual-heat-effect" divided by "theoretical-heat-effect." At low temperatures the extent to which equilibrium is attained in the actual tests is very low. At higher temperatures the approach is closer. Several factors influence the approach: (1) The velocity of the

gases through the fuel bed influences the rate of diffusion at the carbon surface. For low velocities diffusion may retard the reaction. (2) The specific reactivities of the species of carbon utilized differ and decrease in the following order: charcoal, gas coke, foundry coke, and graphite. (3) The rate may drop off with time owing to initial combustion of the more reactive parts of the surface. (4) The rate will decrease with high velocities owing to insufficient contact time. Depending on temperature, 2 to 10 seconds is required for an approach to equilibrium values.

FIG. 6. Effect of temperature on the reaction $C + H_2O$. Percent H_2O undecomposed equals $\dfrac{H_2}{H_2 + H_2O}$.
1. Equilibrium conditions in steam at atmospheric pressure.
2. Actual test in nitrogen saturated with water vapor at 70° C; the carbonization temperature was the same as the reaction temperature. [26]
3. Acual test in standard nitrogen-water vapor mixture using furnace coke. [29]
4. Actual test in standard nitrogen-water vapor mixture using graphite. [29]

(3) $$C + CO_2 = 2CO$$

This reaction is essential in the manufacture of producer gas. It takes place in all

[29] Cassan, H., *Chaleur et ind.*, **18**, 355–64, 406–12 (1937).

combustion processes where more than a very thin fuel bed is maintained; secondary air is required to utilize more completely available heat in the combustion gases. By operating with a thick fuel bed, in an effort to have reaction 3 proceed to practical completion, producers are operated to yield a gas of high carbon monoxide content and low dioxide content.

Boudouard,[30] after whom the reaction is often named, was the first to study the equilibrium in a temperature range from 450 to 1,000° C. After his work, additional data were reported by Mayer and Jacoby,[31] Arndt and Schraube,[32] largely obtained by the static contact method, and by Rhead and Wheeler,[33] obtained by means of a dynamic method. Among other authors contributing to the equilibrium data are included Schenck et al.[34] and Smits.[35]

In some of the tests catalyzers such as finely divided nickel have been used to aid the establishment of equilibrium. Clement and coworkers [36] published a classical piece of work on the Boudouard reaction with direct application to the producer-gas process. Charcoal, coke, and anthracite were used in the investigations, and their reactions with carbon dioxide were studied for temperatures up to 1,300° C with varying

time of contact. Figure 7 is typical for the results obtained with coke. The physical chemistry of the Boudouard reaction was discussed by them at some length. Reaction constants K_1 and K_2 from the expression

$$\frac{d(CO)}{dt} = K_1(CO_2) - K_2(CO)^2$$

were given as follows (time unit, 1 second):

| TEMPERATURE | CHARCOAL | | COKE | | ANTHRACITE | |
°C	K_1	K_2	K_1	K_2	K_1	K_2
800	0.0197	3.03	0			
900	0.154	2.60	0.00231	0.0369		
1,000	0.640	4.71	0.0232	0.359		
1,100	1.495	5.28	0.134	0.530	0.119	1.41
1,200			0.410	0.672	0.237	0.177
1,300			1.483	0 731	0.579	0.202

The irregular variation of K_2 with temperature was attributed to experimental error. The difference in the values of K_2 for different carbons is noteworthy considering that in the reverse reaction lampblack is always formed. Clement assumed that the mass-action law is not strictly applicable because of the simultaneous presence of different forms of carbon. Calculations for the heat of activation gave values of 51,000 calories per gram mole for charcoal, 47,000 for coke, and 32,000 for anthracite. It was pointed out that chemical reaction rate is the controlling factor in this reaction, effects of diffusion being of secondary importance.

Rhead and Wheeler [37] in a later paper also reported reaction-rate constants for the $CO_2 + C = 2CO$ reaction. In following years the above reaction was studied repeatedly in connection with reactions 6, 7, and 8, all involved in the interaction of carbon with air and steam. It was stated by Neumann [38] that reaction 3 does not

30 Boudouard, O., *Bull. soc. chim.*, **21**, 465–7, 713–5 (1899), **25**, 227–30, 833–40 (1901); *Ann. chim phys.*, **24**, 1–85 (1901).

31 Mayer, M., and Jacoby, J., *J. Gasbeleucht*, **52**, 166–94, 238–82, 305–26 (1909).

32 Arndt, K., Henseling, F., Altmayer, V., and Schraube, G., *Nernst Festchrift*, pp. 46–52, 1921.

33 Rhead, T. F. E., and Wheeler, R. V., *J. Chem. Soc.*, **97**, 2178–89 (1910), **99**, 1140–53 (1911).

34 Schenck, R., and Zimmerman, F., *Ber.*, **36**, 1231–51 (1903). Schenck, R., and Heller, W., *ibid.*, **38**, 2139–43 (1905).

35 Smits, A., *ibid.*, **38**, 4027–33 (1905).

36 Clement, J. K., *Univ. Illinois, Bull.* **30** (1909), 47 pp. Clement, J. K., and Grine, H. A., *U. S. Geol. Survey, Bull.* **393** (1910), pp. 15–27. Clement, J. K., Adams, L. H., and Haskins, C. N., *U. S. Bur. Mines, Bull.* **7** (1911), 58 pp.

37 Rhead, T. F. E., and Wheeler, R. V., *J. Chem. Soc.*, **101**, 831–45 (1912).

38 Neumann, K., *Stahl u. Eisen*, **33**, 394–402 (1913); *J. Soc. Chem. Ind.*, **32**, 353 (1913);

FIG. 7. Effect of time of contact, t in seconds, and of temperature on the reaction $CO_2 + C$ in the presence of nitrogen. After Clement, Adams, and Haskins.[**]

go to completion in the short time available for contact, but reaction 8 does. One particularly interesting point raised by Neumann is the reversion of reaction 3 causing decomposition of CO to $CO_2 + C$ after the gases have left the fuel bed. The result of this reaction is a drop in heating value of the gas due to conversion of combustible carbon monoxide into inert dioxide and finely divided solid carbon which is lost to the gas flow. Neumann claimed that the heating value of gas mixtures (producer gas) leaving the fuel bed at 700 to 900° C may decrease 10 to 27 percent while the gas cools down to a final temperature of 400 to 500°. Rapid cooling of the gas to immobilize the equilibrium and high velocity of the gases to reduce the time at high temperature were advocated as means to limit this reduction in heating value. The temperature corresponding to the monoxide/dioxide ratio of the cooled gas is around 600° C, indicating that the rate of the reverse action 3 is too slow below 600° to affect the gas composition further. An approximate relation is given for the frac-

tional decrease in heating value of the gas as follows:

$$1 - \frac{H_6}{H_5} = m \frac{t_5}{c}$$

when the constant $m = 0.14 \times 10^{-3}$, c is the gas velocity in meters per second, t_5 is the temperature (°C) of gas on leaving contact with fuel bed, and H_5 and H_6 are the lower heating value of gas upon leaving fuel bed and the final value, respectively.

The "Neumann reversal" reaction has been discussed by Hudler[39] and by Holgate.[39] However, few additional data have been published since Neumann's paper on this reversal reaction. The extent to which it takes place is somewhat questionable, and further investigation is needed.

Results on the equilibrium of reaction 3 at high pressure have been reported by Jellinek and Diethelm[40] for a temperature range of 800 to 1,000° C and pressures up to 50 atmospheres. Agreement was found between results obtained with graphite and

Z. Ver. deut. Ing., 58, 1482–4, 1501–4 (1914).
Neumann, K., und Le Châtelier, C., Stahl u. Eisen, 33, 1485–7 (1913).

39 Hudler, J., Feuerungstech., 1, 425–7 (1914).
Holgate, T., Gas World, 60, 671–2 (1913).

40 Jellinek, K., and Diethelm, A., Z. anorg. allgem. Chem., 124, 203–29 (1922).

with amorphous carbons. The mass-action law was obeyed at the higher pressures.

Since 1930 the determination of the velocity of reaction 3 at different temperatures has been advanced materially. Dubinsky [12] determined the rate of oxidation of brush carbon spheres by carbon dioxide with the type of apparatus described by Tu and Hottel. Between 1,500 and 1,700° K, he found a rapid increase in reaction rate from values of the order of 0.05×10^{-3} to 0.3 gram per square centimeter per second. Drakeley [41] studied the $C + CO_2$ reaction between 950 and 1,100° C and expressed the reaction rate $(d \, [CO]/dt)$ as $K_1(CO_2) - K_2(CO)^2$, thus indicating the influence of the reverse reaction. An effort was made to express reactivity of the different fuels in terms of constant K_1. The relations between the two K values and temperature appeared somewhat indeterminate, probably owing to surface effects; K_2 also varied with the type of fuel used and had an abnormal temperature coefficient.[42] Evidence of the complexity of the seemingly simple reaction between carbon dioxide and carbon has also been offered by Broom and Travers.[43] In their opinion the reactions take place in two phases:

$$CO_2 + C = CO + C_xO_y$$

$$C_xO_y = CO + C$$
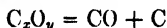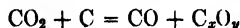
supporting to some extent the early theories of Rhead and Wheeler, Sihvonen, and many others. The tendency of carbon to cover itself with an oxygen film has been discussed from a different angle by Verwey and deBoer [44] and also by Klemenc [45] et al.

Blakeley and Cobb,[46] using a method previously developed by Branson and Cobb,[47] studied the reduction of a stream of carbon dioxide diluted with nitrogen by coke and other forms of carbon. The coke, sized between $\frac{1}{6}$ and $\frac{1}{10}$ square inch mesh, was introduced into a tube $\frac{7}{8}$ inch in internal diameter. The gas velocity was varied to a maximum rate of 25 liters per hour, and the temperature was also varied. The results indicated that practically complete carbon dioxide decomposition was attained for 1 second reaction time at 1,250° C and for $\frac{1}{10}$ second reaction time at 1,550° C. At these temperatures there was no difference in reactivity between the least (graphite) and the most reactive (charcoal) type of carbon used. Great differences in reactivity were evident at lower temperatures (see also Fig. 7). The specific reactivity K was expressed as the reciprocal of the quantity of coke in 10-gram units required to decompose 20 percent of a stream of carbon dioxide at a 5-liter-per-hour rate under the experimental conditions stated. An equation was given to calculate this reactivity from data for diluted carbon dioxide mixtures and other variable conditions. Curves, in which the specific reactivity is plotted against the time of exposure at 1,000 and 1,400° C, as well as the specific reactivity against temperature, are shown in Figs. 8, 9, and 10. The time curves show a decrease of K with time due to initial combustion of more readily oxidized portions of the surface. The reactivity of carbon to water parallels usually the reactivity of carbon to carbon dioxide.

[41] Drakeley, T. J., *J. Soc. Chem. Ind.*, **50**, 319-30T (1931).

[42] Cf. ref. 36.

[43] Broom, W. E. J., and Travers, M. W., *Proc. Roy. Soc. (London)*, A**135**, 512-37 (1932).

[44] Verwey, E. J. W., and deBoer, J. H., *Rec. trav. chim.*, **55**, 675-87 (1936).

[45] Klemenc, A., Wechsberg, R., and Wagner, G., *Z. Electrochem.*, **40**, 488-9 (1934).

[46] Blakeley, T. H. and Cobb, J. W., *Inst. Gas Engrs., Commun.* **104**; *Gas World*, **101**, 452-5, 498-9, 612-3 (1934).

[47] Branson, W. R., and Cobb, J. W., *Trans. Inst. Gas Eng.*, **76**, 357-71 (1926-7).

A great deal of similar work has been done on the $CO_2 + C$ reaction.[48] All this work constitutes part of an extensive lit-' erature principally concerned with the determination of relative reactivity of fuels. (See also Chapter 24.)

An elaborate study concerning the $CO_2 + C$ reaction was made by Mayers.[49] In an effort to define the experimental
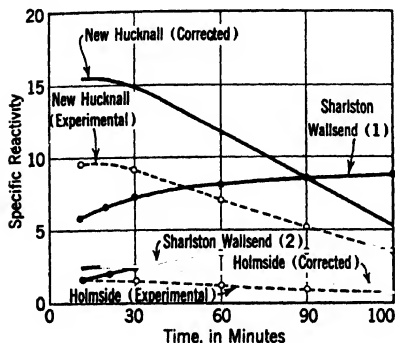
FIG. 8. Specific reactivity at 1,000° C of cokes from bituminous coals. The corrected curves are on a comparable basis.[49]

conditions as closely as possible, a cylinder of Acheson graphite, 21.3 millimeters outside diameter, 14 millimeters long, sealed between sillimanite bodies was studied under variable conditions of gas velocity and temperature.

The reaction was conducted at gas-flow rates high enough to eliminate any diffu-

48 Agde, G., and Schmitt, H., *Brennstoffchem.*, 8, 1921–3 (1927) ; *Z. angew. Chem.*, 40, 1003–8, 1027–32 (1927). Nettlenbusch, L., *Brennstoff-chem.*, 8, 37–41 (1927). Jones, J. H., King, J. G., and Sinnatt, F. S., *Dept. Sci. Ind. Research* (*Brit*), *Fuel Research, Tech. Paper* 18 (1927), 32 pp. Cobb, J. W., and Parker, A., *Trans. Inst. Gas Engrs.*, 79, 58–101 (1929). Dent, F. J., and Cobb, J. W., *J. Chem. Soc.*, 1929, 1903–12. Key, A., and Cobb, J. W., *J. Soc. Chem. Ind.*, 49, 439–44T, 454T (1930). Cassan, H., *Chaleur et ind.*, 18, 355–64, 406–12 (1937).

49 Mayers, M. A., *J. Am. Chem. Soc.*, 56, 70–6 (1934), 61, 2053–8 (1939).

sional effects. At temperatures from 850 to 1,306° C, the rate of carbon monoxide formation increased from 1.5 to 500 cubic millimeters per square centimeter surface
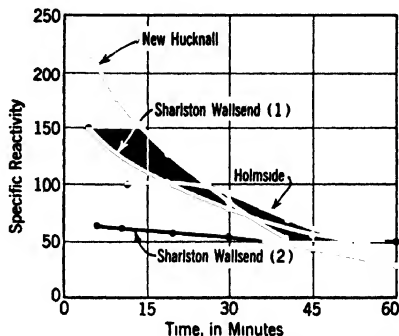
FIG. 9. Specific reactivity at 1,400° C of cokes from bituminous coals.[49]

per second. In these tests the gas-flow rate ranged from 0.7 to 16.7 liters per minute of carbon dioxide, linear velocities ranging from 6 to 34 centimeters per second.
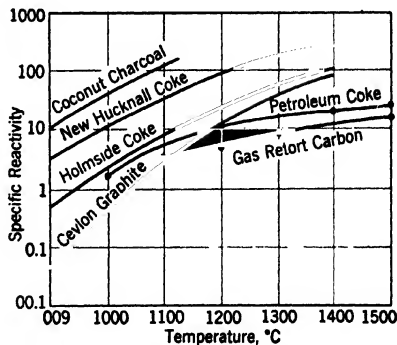
FIG. 10. Specific reactivity of various types of carbon.[49]

The observed rates followed two simple equations for A, the reaction rate, with an apparent discontinuity at 950° C indicated by an increase in reactivity gradient. The

two equations correlating the observed values of A were the following:

Below 950° C (850 to 950°),

$$\log A = 3.40 - \frac{32,360}{4.575T}$$

Above 950° C (950 to 1,300°),

$$\log A = 5.07 - \frac{38,700}{4.575T}$$

The discontinuity was attributed in the 1934 paper to a change in nature of the C_xO_y complex.[50] Similar discussions have been given by several other authors.[51]

The proposed theory is that the reaction $CO_2 + C = CO + C_xO_y$ complex takes place at low temperatures (below 950°) with a rate of decomposition of the complex to carbon and carbon monoxide lower than that of the reaction itself. At increasing temperatures, the decomposition of the complex takes place more rapidly, and above 950° the two reactions add up to $CO_2 + C = 2CO$, leaving a clean surface for the reaction. It is evident that below 950° the reaction between carbon dioxide and carbon will eventually slow down to the rate of the C_xO_y complex decomposition rate as soon as the entire surface is covered by the complex.

In the 1939 paper, Mayers studied high-temperature coke as well as graphite in experiments conducted in somewhat different manner. The furnace tube contained a solid mullite boat with a recess in the upper portion. For the investigation either granular or monolithic samples of carbon were used, including natural or artificial graphite between 16 and 20 U. S. mesh, as well as four samples of coke prepared at a final temperature of 1,000° C. Generally the reaction rates were found to decrease with time. Furthermore, the rates varied with the thickness of the granular samples (difference in level of top and bottom of recess in boat). For the monolithic samples (graphite) the limiting value for pure surface reaction was approached. Evidently the interior surface of the carbon contributed its share to the reaction. Even monolithic artificial graphite (Acheson) showed the effect of a 29 percent pore volume. The use of a porosity correction made necessary by the perfusion of the body of the carbon by the oxidizing gas explained a number of previous inconsistencies in results. The temperature coefficient determined in these tests for graphite agreed with that of Blakeley and Cobb.[46] Upon the porosity basis, abnormal results of Davis and Hottel[14] were explained as well as differences between rate determinations at normal pressure and in vacuo.[51]

A uniform relationship between reaction rate expressed in micromoles of carbon monoxide formed per cubic centimeter per second and temperature was found at temperatures between 1,200 and 800° C. On account of the volume correction, the accuracy of the rate determination was considered to be less than 20 percent. The heat of activation for artificial graphite was 52,000 calories and that for natural graphite 44,000 calories, the accuracy of the latter being less due to mineral impurities. Values as now accepted by Mayers for the reaction rate R for the range given follow a linear relation between $\log R$ and $1/T$. Approximate values which apply to granular graphite as well as coke are 55 micromoles of carbon monoxide per cubic

50 Cf. ref. 43.

51 Rhead, T. F. E., and Wheeler, R. V., J. Chem. Soc., 103, 461–89, 1210–4 (1913). Langmuir, I., J. Am. Chem. Soc., 37, 1139–67 (1915). Lowry, H. H., and Hulett, G. A., ibid., 42, 1408–19 (1920). Eucken, A., Z. angew. Chem., 43, 986–93 (1930). Meyer, L., Z. physik Chem., B17, 385–404 (1932). Sihvonen, V., Ann. Acad. Sci. Fennicae, A34, No. 7 (1932), 29 pp.; Z. Elektrochem., 40, 456–60 (1934). Martin, H., and Meyer, L., ibid., 41, 136–46 (1935). Ruff, O., Trans. Faraday Soc., 34, 1022–33 (1938).

centimeter per second at $T = 1,428°$ K (1,155° C), and 0.35 at $T = 1,111°$ K (838° C).

(8) $\qquad CO_2 + H_2 = CO + H_2O$
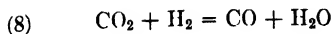
This reaction is the only homogeneous gas reaction among those discussed hitherto. It is commonly called the "water-gas reaction" owing to its importance in the manufacture of the basic constituent of "blue" water gas, a mixture of carbon monoxide and hydrogen. · The reaction occurs in all processes of partial or complete combustion if water is present. It serves to establish a ratio between carbon monoxide and dioxide, and hydrogen and water, depending on the temperature and concentrations of the components.

The rate of water-gas reaction has been discussed at some length by Dolch,[25] who reviewed the work of other investigators. Although, in most combustion and gas-making processes, the water-gas-reaction equilibrium appears to be established at fairly low temperature, experiments of Dolch[52] showed that a temperature of 1,000° C was required before carbon dioxide and hydrogen would react and equilibrium was not reached until 1,400°. In his tests, a quartz tube filled with quartz pieces was used. An entirely different behavior was observed, however, when the reaction rate was determined in the presence of a carbon surface such as is normally present in a bed of combustible fuel. Dolch showed that equilibrium was reached for the water-gas reaction at temperatures as low as 700° C in the presence of charcoal or lignite coke, and at 1,000° C in the presence of less active forms of carbon such as blast-furnace coke. The contact time in all the experiments was of the order of 1 second.

Similar figures were given by Terres,[26] who stated that, in the absence of carbon, the establishment of equilibrium required 50 and 70 seconds at 600 and 1,200° respectively; the presence of carbon reduced this time four to tenfold.

Some experimental work has been done to study the mechanism of this surface effect. Several authors[53] have attributed it to the ash constituents of the carbon. It should be emphasized that the catalytic surface effect of the carbon takes place with or without chemical attack of the carbon surface. Lack of chemical attack of the surface is indicated by constant volume of the reacting gases. The apparent difference in catalytic activity with different types of coke is very significant.

CATALYTIC EFFECTS

Although briefly mentioned in connection with the water-gas reaction the subject of catalysis requires additional mention. Considerable work has been done on the catalytic effects of different chemicals on the various reactions between carbon, oxygen, and water vapor. Such work is of direct importance in the producer and in the water-gas-set operation in so far as it enables the operator to influence the operating rate, gas composition, and other important factors.

Taylor and Neville[54] were among the first to investigate the effect of various catalytic agents upon the reactions between carbon and steam at temperatures from 490 to 570° C, steam being passed over the charcoal containing the catalyst in a Pyrex glass reaction chamber. Considerable catalytic effects were observed with sodium or

[52] Dolch, P., *Brennstoff-Chem.*, **14**, 261–3 (1933).

[53] Gwosdz, J., *Z. angew. Chem.*, **31**, 137–40 (1918). Neumann, B., Kröger, C., and Fingas, E., *Gas- u. Wasserfach*, **74**, 565–72 (1931).

[54] Taylor, H. S., and Neville, H. A., *Science*, **53**, 577 (1921); *J. Am. Chem. Soc.*, **43**, 2055–71 (1921).

potassium carbonates, the latter being the more active. With either, the maximum efficiency was obtained when 20 percent by weight of the catalytic agent was incorporated in the reaction mixture. Barium hydroxide, borax, water glass, and soda lime were ineffective. Iron oxide was found to be ineffective although it is known to catalyze the $CO + H_2O$ gas reaction. From this it was concluded that probably the catalytic effect of alkali carbonates was due to the acceleration of the $C + CO_2 = 2CO$ reaction. Experiments indicated that catalysis of the reaction $C + CO_2 = 2CO$ took place at 570° C using the alkali carbonates and nickel. Nickel was found to be the more active agent. Nickel also catalyzes the reaction $C + H_2O$ but loses activity rapidly. Potassium carbonate also catalyzes the $2CO = CO_2 + C$ reaction. The mechanism of the catalytic activity was associated with the influence of the catalytic agent upon the C_xO_y complex surface compounds.

Cobb and coworkers[55] in England published a series of papers on similar work in which again the superiority of sodium carbonate as a catalyst was demonstrated. This work was partly done with oxygenated blast air. The catalyst caused the reaction temperature to be some 100° C lower and to increase the carbon monoxide content of the gases. Further work on the same subject has also been published by White and others.[56] Above 750° C it was found that

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a reaction $2C + Na_2CO_3 = 2Na + 3CO$ can take place, so that at temperatures above 1,025° C a stream of vapor would evolve, the stream being adequate to rupture the stagnant gas film on the carbon particles. In this manner the $C + CO_2$ reaction is accelerated. Neumann and associates[57] explained the effect of alkali carbonates in a similar manner. The sodium vapor was supposed to be reoxidized and again form
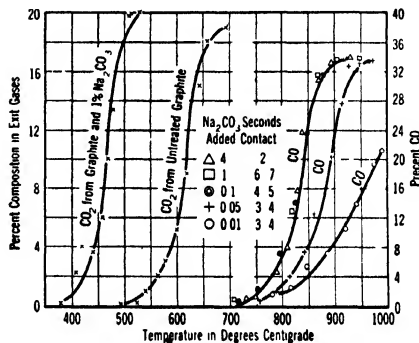
Fig. 11.   Influence of additions of sodium carbonate on the composition of gases obtained from the interaction of graphite and dry air. After Weiss and White.[56]

sodium carbonate in the upper cooler portions of the fuel bed.

With additions of sodium carbonate as low as 0.01 percent by weight, a noticeable acceleration of carbon dioxide reduction in fuel beds was obtained with 2 to 7 seconds contact time (Fig. 11). With 0.1 percent and more of sodium carbonate in the fuel bed, equilibrium was obtained in the $CO_2 + C$ reaction at 900° C with 33 percent carbon monoxide in the reaction gas,

55 Marson, C. B., and Cobb, J. W., Gas J., 175, 882–91 (1926). Cobb, J. W., et al., ibid., 178, 895–912 (1927). Sutcliffe, J. A., Cobb, J. W., Branson, W. R., and Dent, F. J., Fuel, 6, 449–73 (1927). Dent, F. J., Gas World, 89, 453–6 (1928); Gas J., 184, 199–200 (1928), 186, 766 (1929). Sutcliffe, J. A., Dent, F. J., and Cobb, J. W., Gas World, 88, 709–12 (1928).

56 Hollings, H., and Siderfin, N. E., J. Soc. Chem. Ind., 46, 76–84T (1927). Jones, J. H., King, J. G., and Sinnatt, F. S., Dept. Sci. Ind. Research (Brit.) Fuel Research, Tech. Paper 25 (1930), 42 pp. Fox, D. A., and White, A. H.,

Ind. Eng. Chem., 23, 259–66 (1931). Weiss, C. B., and White, A. H., ibid., 26, 83–7 (1934). Fleer, A. W., and White, A. H., ibid., 28, 1301–9 (1936). Askey, P. J., and Doble, S. M., Fuel, 14, 197–201 (1935). Kröger, C., and Mellhorn, G., Brennstoff-Chem., 19, 157–69 (1938).

57 Neumann, B., Kröger, C., and Fingas, E., Z. anorg. allgem. Chem., 197, 321–38 (1931).

graphite being the source of carbon, and dry air the source of oxygen. For graphite treated with 1 percent sodium carbonate, 2 seconds contact time sufficed to give 31 percent carbon monoxide at 850° C, whereas only 25 percent was obtained from untreated graphite at 1,050° C.

With foundry coke larger percentages of sodium carbonate were required because of the tendency of sodium carbonate to react with the ash to form silicates. Addition of 5 percent sodium carbonate was sufficient to give material acceleration in the carbon monoxide production. At 880° with 5 percent sodium carbonate a gas containing 1.6 percent carbon dioxide, 34.0 percent carbon monoxide, and 11.4 percent hydrogen was made, and at 1,090° the same coke with no catalyst gave 9.8 percent carbon dioxide, 19.8 percent carbon monoxide, and 8.6 percent hydrogen. Besides accelerating carbon dioxide reduction, the addition of sodium carbonate lowered the reaction temperature for graphite and air by 150°, which resulted in complete oxygen consumption from air at 525° instead of at 675°. The active fuel bed used in these tests was from 250 to 300 millimeters deep.

Kröger[58] has claimed that for reactions 1 and 3 heavy metal oxides of low heat of oxide formation are active, and for reaction 6 oxides of intermediate heat of formation serve as catalysts. Mixed catalysts such as alkali carbonate plus cobalt or copper oxide were advocated. The theory proposed was that such combinations form surface alloys and reduce the volatility of the alkali metal. Graphite activated with such a catalyst gave 30 percent steam decomposition at 600° C, and 70 percent at 700° C, while potassium carbonate alone gave 15 and 45 percent respectively. The

effect of the catalysts was relatively less at higher temperatures and also with more reactive fuels.

A somewhat different approach to the study of these catalytic effects has been pursued by a number of authors[59] studying the decomposition of carbon monoxide. Tropsch found that at 400° C using a flow of 400 cubic centimeters of carbon monoxide per hour there was 36.4 percent decomposition of monoxide to $CO_2 + C$ in the presence of nickel, 10.4 percent in the presence of reduced ferric oxide, 2.3 percent with "ferrum reduction," and less than 1 percent with zinc or manganese oxide, chromic oxide, aluminum oxide, barium sulfate, tinned iron, magnesium oxide, or copper. This type of reaction tended to form metal carbides, in accord with the results of Tutiya[59] and Bahr[59] using carbides of iron, nickel, molybdenum, and cobalt.

The carbon dioxide decomposition reaction is also influenced by various refractories, the reaction resulting in graphite deposition in interstices of brickwork. Hubbard and Rees[60] showed that temperatures from 260 to 300° C for alumina, calcined slag, and ferric oxide caused carbon monoxide decomposition. A temperature of 520° was necessary to obtain the same reaction for silica. It was believed that ferric oxide is one of the more active catalyzers.

Among the more recent publications on catalysis of carbon reactions is an article

[59] Tropsch, H., and von Phillipovich, A., *Ges. Abhandl. Kenntnis Kohle*, **7**, 44–5 (1922–3). Meyer, G., and Scheffer, F. E. C., *Rec. trav. chim.*, **46**, 754–62 (1927). Tutiya, H., *Bull. Inst. Phys. Chem. Research Tokyo*, **8**, 609–13 (1929), **10**, 556–62, 951–73 (1931), **11**, 1136–49 (1932). Bahr, H. A., and Jessen, V., *Ber.*, **63B**, 2226–37 (1930).

[60] Hubbard, D. W., and Rees, W. J., *Trans. Ceram. Soc.*, **28**, 277–307 (1929).

[58] Kröger, C., *Angew. Chem.*, **52**, 129–39 (1939).

by Laupichler [61] in which the mechanism of the surface catalysis of the $CO + H_2O = CO_2 + H_2$ reaction was analyzed, and the effects of diffusion separated from truly catalytic effects.

Calling R_1 the velocity coefficient of the catalyzed reaction in the expression

$$W_1 = R_1C_{2m}(C_1' - C_1'')$$

in which W_1 = moles of gas diffusing per second per square centimeter of catalyzer surface, $C_{2m} = H_2O$ concentration, C_1' = actual CO concentration, and C_1'' = equilibrium CO concentration, it was calculated that

$$\log_{10} R_1 = \frac{-5{,}640}{Tm} + 11.71$$

in which Tm = the mean temperature of the catalyst. In the range of 460 to 570° C, $R_{T+10}/R_T = 1.23$ when the diffusion resistance was considered negligible. By means of the R_1 values, for which the method of determination was given, different catalysts could be compared. The heat of activation of the heterogeneous re-

(11) $C_{gr} + 2(H_2)_g = (CH_4)_g$ $\Delta H°$ 298.1 = −18,050 calories per mole

                                                $\Delta F°$ 298.1 = −12,280 calories per mole

(12) $(CO)_g + 3(H_2)_g = (CH_4)_g + (H_2O)_g$ $\Delta H°$ 291 = −49,505 calories per mole
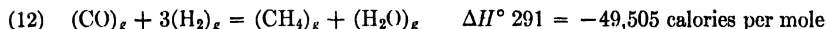
                          $\Delta F°$ = −34,000 calories per mole

action on the catalyst surface was 25,800 calories per mole.

Sebastian [62] has repeated previous tests using 40- to 60-mesh coke and adding up to 5 percent sodium carbonate or molybdenum sulfide on silica gel and 1 percent of sodium or ammonium molybdate or sodium phosphate. As usual sodium carbonate was found most active. It was claimed that, whereas with pure coke the reaction $C + O_2$ is of first order, the heterogeneous catalyzed reaction is of zero order. The method used for the tests was similar to that described previously for ignition temperature determinations. The determinations indicated no change in heat of activation of the reaction in the presence of 3 percent sodium carbonate. However, it appeared that the surface oxide layer on the coke was changed in the presence of catalyst. Ferric oxide in 10 percent concentrations, mixed wet or dry, had no effect on the $C + O_2$ reaction.

METHANE FORMATION

Methane is nearly always present in producer gas, its origin being partly due to the volatile matter of the fuel, which liberates methane upon heating, partly to its formation from carbon, hydrogen, or water, since all are present in the reaction chamber.

Reactions involved in the formation of methane include the following:

The data given here are derived from work by Rossini, Kelley, and Austin and Day,[63] since the values of the *International Critical Tables* appear to be somewhat different and less accurate.

A plot of log K of reaction 11 versus T (Fig. 12) shows that methane formation is well within the realm of possibility at the temperature prevailing in producer fuel

61 Laupichler, F. G., *Ind. Eng. Chem.*, **30**, 578–86 (1938).

62 Sebastian, J. J. S., *Symposium on Solid Fuels*, Am. Chem. Soc. Meeting, Boston, 1939, pp. 37–40.

63 Rossini, F. D., *J. Chem. Phys.*, **6**, 569 (1938). Kelley, K. K., *U. S. Bur. Mines, Bull.* **407** (1937), 66 pp. Austin, J. B., and Day, M. J., *Ind. Eng. Chem.*, **33**, 23–31 (1941).

beds. Higher temperatures tend to displace the equilibrium of reaction 11 toward the left (exothermic reaction); higher pressures tend to shift it toward the right. Hence low temperatures and high pressures are requisites for maximum methane production. Early work on methane formation in producer fuel beds was mentioned by Clement, Adams, and Haskins.[36]
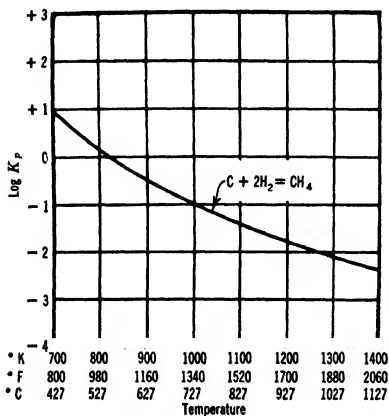
FIG. 12. Variation of log K_p with temperature for the reaction $C + 2H_2 \rightarrow CH_4$.

As to the kinetics of methane formation from the reaction $C + 2H_2$, some very pertinent information has been obtained in experiments on the interaction of cokes and coals with hydrogen by Dent and co-workers[64] in England.

Passing hydrogen through a 9.5-inch layer of coke in a tube 1 inch in internal diameter (weight of charge 25 to 40 grams), at a rate of 20 liters per hour (1.3 seconds contact time at atmospheric pressure), the rate of hydrogenation of the coke was established at different pressures. Except for some methane and hydrogen evolution from the coke in a nitrogen

[64] Dent, F. J., Blackburn, W. H., and Millett, H. C., *Inst. Gas Engrs., Commun.* **167** (1937), 47 pp., **190** (1938), 69 pp.

stream at 500 to 800° C due to the volatile matter of the fuel, the formation of methane in the hydrogen stream was distinct. With a coke made from Yorkshire coal at 450 to 500° in nitrogen a 23.0 therm yield of hydrogen, a 14.7 therm yield of methane, and a total hydrocarbon yield of 16.3 therms per ton of coke at atmospheric pressure. In hydrogen at atmospheric pressure, at 800° C, there were obtained 1.3 therms of hydrogen and 33.8 therms of hydrocarbons; at 5 atmospheres in hydrogen, 92.1 therms total; at 10 atmospheres, 132.9 therms; at 25 atmospheres, 202.5 therms; at 50 atmospheres, 276.0 therms; at 100 atmospheres, 331.2 therms. Maximum Btu values of the gas produced were: at 1 atmosphere, 345 Btu per cubic foot; at 10 atmospheres, 500 Btu; at 100 atmospheres, 914 Btu. Methane began to appear at 500° C, and as much as 72 percent of the coke was gasified in the pressure experiments.

At low pressures, the reactions proceeded most rapidly at 500 to 550° C; at higher pressures at 700 to 750°. Other fuels gave similar yields, although the initial hydrogenation temperature varied to some extent. Mixtures of carbon monoxide and hydrogen gave similar results. Later tests showed that maximum yields of gaseous hydrocarbons could be obtained at 900 to 950° C. Coals carbonized at 450 to 500° C gave 500 to 600 therms of gaseous fuel per ton with calorific value above 500 Btu per cubic foot, 70 to 85 percent of the carbon being gasified. With coke prepared at 800° the hydrogenation at 900° was especially advantageous; hydrogenation at 800° gave 140 therms of gaseous hydrocarbon, at 900° C 520 therms, the pressure being 50 atmospheres. The presence of alkali carbonate accelerated the hydrogenation, especially at the lower temperatures: at

800°, 140 therms was produced without alkali; at 800°, 463 therms with 3 percent sodium carbonate in the coke. The percentage of methane made in some of the coke experiments reached equilibrium in some tests. The percentage of methane obtained at lower pressure and lower temperature can be as high as at high pressure and temperature as long as the coke is sufficiently reactive. Many interesting details are given in these reports.

As to equilibrium and rate of reaction 10, the data in the literature are inadequate and the impression is obtained that the interaction of carbon with hydrogen in fuel beds is at least as important as the conversion of $CO + 3H_2$ (or of $CO_2 + 4H_2$) to CH_4. Dent cited some experiments in which mixtures of 12 percent carbon dioxide, 3 percent carbon monoxide, 27 percent hydrogen, and 58 percent steam were passed over crushed silica at 50 atmospheres, as well as over different types of coke. With silica very little methane was formed: 1.3 percent at 600°, 1.9 at 700°, and 1.1 at 800°. With high-temperature retort coke or graphite, from 4.4 to 10.4 percent methane was obtained, and the addition of either sodium carbonate or ferric oxide to the coke had no effect. The best results, up to 20 percent methane in the carbon dioxide-free gas, resulted from the use of coke prepared at 700° from Leicestershire coal.

It is realized, of course, that reactions like 12 always take some part in the methane formation, especially if suitable catalysts for this type of reaction are present. Homogeneous gas reactions generally are faster than reactions between gases and solids. On the other hand, reaction 12 as written requires interaction of four molecules and for that reason can be expected to be slow. Considerable early work on the formation of methane from carbon monoxide and hydrogen under the influence of catalysts was done by Vignon.[65]

The formation of methane in producer and water-gas manufacture needs further investigation.

THEORY OF GAS REACTIONS

In surveying the status of present knowledge concerning such fundamental gas reactions as 1, 2, 3, 6, 7, and 8, it is obvious that the equilibrium data on these reactions are well established. Since 1920 adequate data on specific heats, heats of reaction, and determination of equilibrium constants at different temperatures have been obtained and coordinated to give a consistent set of thermodynamic equations.

The data available on the rate of approach of the equilibrium condition if possible from both sides are fewer in quantity as well as quality. It can hardly be asserted that the study of the kinetics of any of the reactions has been exhausted.

With reactions 1 and 2 the decision between carbon monoxide, carbon dioxide, and C_xO_y as primary product has not definitely been made for all temperature and pressure conditions. Since the equilibria of these reactions lie well over on the right-hand side at normal working temperatures no complication with reverse reaction arises. It seems fairly well established that the oxidation of carbon is a first-order reaction and that the reaction rate at temperatures above 1,000° is solely a function of the rate of removal of the oxidation products, monoxide or dioxide. At lower temperatures where chemical resistance plays a role, catalysts have been found that accelerate the rate of reaction although it still remains somewhat question-

65 Vignon, L., *Compt. rend.*, **156**, 1995-8 (1913), **157**, 131-4 (1913).

able whether their effect is a chemical or a physical one.

With reactions such as 3, 6, and 7 the picture is not quite as simple as for 1 and 2. All these reactions are heterogeneous gas reactions, and the equilibria of reactions 3, 6, and 7 lie within range of the usual experimental temperatures. Taking the reaction $C + CO_2 = 2CO$ as an example of this type, equilibrium can be approached from two sides. In measuring the rate of the reaction when proceeding from left to right the effect of the reverse reactions must necessarily be observed. For a rate of change of carbon dioxide pressure expressed as dp_{CO_2}/dt it follows that at any temperature

$$-\frac{dp_{CO_2}}{dt} = K_1 p_{CO_2} - K_2 p^2_{CO} = \frac{1}{2}\frac{dp_{CO}}{dt}$$

$$\frac{K_1}{K_2} = K_p$$

where K_1 and K_2 are velocity constants and K_p is the equilibrium constant at the same temperature. Whereas K_p is related to $-\Delta F$, the change in free energy of the reaction, by

$$-RT \log_e K_p = \Delta F$$

and to the heat of reaction $-\Delta H$ by

$$\frac{d \log_e K_p}{dT} = \frac{\Delta H}{RT^2}$$

there is no such simple set of equations for K_1 or K_2. It has, however, been found experimentally that generally an equation of the following type applies:

$$\frac{d \log_e K_1}{dT} = \frac{A_1}{RT^2}$$

In the integrated form, this becomes

$$K_1 = Be^{-A_1/RT} \quad \text{(Arrhenius equation)}$$

In this the constant A_1, determining the rate of change of K_1 with temperature, has the dimension of a heat quantity and has been called the "heat of activation." A_1 is assumed to represent the (semi-empirical) energy (heat) required to convert the reacting molecules (solid or gaseous) to an activated stage from which the actual reaction can proceed. Catalysts may be of such a nature as to reduce the value of A_1 and hence cause the reaction to take place at lower temperatures. It is obvious that

$$A_1 - A_2 = \Delta H$$

In order to obtain a complete picture of the kinetics of a reaction like 3, constants should be determined to fill out Arrhenius equations for both K_1 and K_2 assuming that the reaction rate is determined by temperature principally. By measuring rates for low values of p_{CO} or for low values of p_{CO_2} results for K_1 and K_2 can be segregated by extrapolations to p_{CO} or $p_{CO_2} = 0$. Diffusion functions in such an analysis are enclosed in the constants of the Arrhenius equation. Another very important item which is included in that equation under B is the so-called reactivity of the solid phase. This reactivity, included in the original K_1, represents the activity p_C of the solid phase, which might well be written in as

$$-\frac{dp_{CO_2}}{dt} = K_1' p_C p_{CO_2} - K_2 p^2_{CO}$$

With the use of a solid phase (carbon) in different physical conditions the activities can be compared and measured on a common scale.

It is rather astonishing to see how seldom this simple set-up for the investigation of heterogeneous gas reactions has been followed. The one outstanding example of development of an equation of the Arrhenius type, including solid-phase activity and diffusion effects, has been given by Hottel and Parker [14] for reaction 1 in a limited range.

Data on "reactivity" of carbon species and on reaction rates are generally badly confused. Reaction constants of almost any kind of dimension can be found; reactivity is expressed in anything from heat units to seconds and centimeters. The effect of the K_2 of the reverse reactions is often conveniently ignored. All this contributes to lack of depth in the information obtained and lack of applicability of the data to general cases. In a few instances such shortcomings have been pointed out in the past.[36, 41] A thorough revision of the field of reactivity and rate determination is badly needed for almost all the reactions under discussion. One unfortunate consequence of the present situation is that sometimes elaborate physical explanations of irregularities found in experimental data are required to cover up inadequate theoretical grounds.

To mention a few subjects that require further study: (1) reverse of reactions 6 and 7; (2) further study of reaction 3 reversed with and without catalyzer; (3) extension of the study of reaction 1 to higher gas velocities; (4) development of a generally acceptable Arrhenius equation for reactions 3, 6, and 7; (5) mechanism of factors involved in the "reactivity" of different forms of carbon, including the effect of chemical structure, pore structure, etc.; and (6) development of a theoretically correct standard expression for reactivity.

Producer Reactions [66]

The reactions taking place in a gas producer represent the making of producer

[66] Allen, H., *Modern Power Gas Producer Practice and Applications,* Technical Publishing Co., London, 1908, 326 pp. Dowson, J. E., and Larter, A. T., *Producer Gas,* Longmans, Green & Co., New York and London, 3rd ed., 1912, 319 pp. Le Châtelier, H., *Le chauffage industriel,* Dunod, Paris, 1920, 536 pp. Gwosdz, J., *Generatorgas,* W. Knapp, Halle, 1921, 191 pp.; Kohl-

gas. Producer gas is a gas with carbon monoxide as the principal combustible constituent, the carbon monoxide being the result of incomplete combustion of a carbonaceous fuel.

When a carbonaceous fuel is exposed to reaction with gases containing oxygen at temperatures above the ignition temperature of the fuel there result two principal reactions correlated by two additional ones:

(1) $$C + O_2 = CO_2$$

(2) $$C + \tfrac{1}{2}O_2 = CO$$

(3) $$CO_2 + C = 2CO$$

(4) $$CO + \tfrac{1}{2}O_2 = CO_2$$
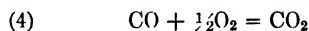
Reaction 1 takes place as long as the oxygen concentration is adequate, and any carbon monoxide formed will be oxidized further as shown by reaction 4. Reaction 1 has the highest heat of reaction, 94,390 calories per mole at 291° K; the formation of carbon monoxide by reaction 2 is accompanied by the evolution of only 26,490 calories per mole at the same temperature.

It depends altogether upon the mode of contact of fuel and oxygen whether carbon dioxide or the monoxide will be the principal product of combustion. In thin, shallow fuel beds, so proportioned that the oxygen of the blast air is reduced to a low

enwassergas, W. Knapp, Halle, 1930, 606 pp. Rambush, N. E., *Modern Gas Producers,* Benn Bros., London, 1923, 568 pp. Trenkler, H. R., *Die Gaserzeuger,* J. Springer, Berlin, 1923, 378 pp. Wheeler, R. V., *Producer Gas and Gas Producer Practice,* Fuel Publications, London, 1923, 102 pp. Korevaar, A., *Combustion in the Gas Producer and the Blast Furnace,* Lockwood, Crosby, & Son, London, 1924, 177 pp. Haslam, R. T., and Russell, R. P., *Fuels and Their Combustion,* McGraw Hill Book Co., New York, 1926, 807 pp. Morgan, J. J., *American Gas Practice,* J. J. Morgan, Maplewood, N. J., 1931, Vol. I, 969 pp. Guillon, H., *Les gazogènes, théorie, pratique, controls,* Chaleur et industrie, Paris, 1939. Brückner, H., *Handbuch der Gasindustrie, Generatoren,* R. Oldenbourg, Munich, 1940, 304 pp.

but positive value while passing through the fuel bed, the dioxide is the principal product. In such fuel beds, the heat evolution is maximum; this type of fuel bed is used in heating furnaces. Small amounts of carbon monoxide formed are often burned up by secondary air admitted above the fuel bed. The maximum thickness for these fuel beds is of the order of 4 inches.

If the fuel bed is thicker than this value a second reaction takes place; the carbonaceous fuel bed heated up by the carbon dioxide-containing gases resulting from reaction 1, as well as by radiation and convection from the underlying fire, will react with the carbon dioxide according to reaction 3 with secondary production of carbon monoxide. Reaction 3 is accompanied by the absorption of 41,410 calories per mole (291° K). Hence, while reaction 3 takes place, the gases cool until, owing to lower prevailing temperatures, reaction 3 stops and the gases leave the fuel bed with the monoxide and dioxide content corresponding to the outcome of reaction 3 at the prevailing temperature and time of contact.

A number of secondary reactions take place at the same time: (1) the heat of the gases causes carbonization, driving out volatile matter and moisture from the freshly charged upper layers of the fuel bed; and (2) for the more common type of producer it is customary to add moisture in the form of steam to the blast air with the result that reactions such as the following take place:

(6) $C + H_2O = CO + H_2$

(7) $C + 2H_2O = CO_2 + 2H_2$
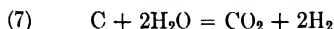
both having negative heat values, 31,340 and 21,270 calories per mole, respectively. This absorption of heat tends to lower the temperature of the fuel bed and is instrumental in preventing fusion of the ash residue of the fuel to large clinker. Thus discharge of ashes from the producer is simplified. The use of steam in the air blast is common, and so-called air producer gas, made from air and fuel only, is seldom made.

When thick fuel beds as described here are confined in a closed space and the gas produced is collected for use separate from the fuel bed, the apparatus is then designated as a gas producer, the gas, as a producer gas.

The gas is sometimes used directly without cooling, and quite often it is cooled and cleaned. The conversion of the heating value of a solid fuel to heat available in a gaseous fuel is consequently expressed either as hot efficiency, which includes the sensible heat of gas, or as cold efficiency, including only the heat of combustion (potential heat) of the cold gas.

Typical of producer operations is the continuity of gas production as compared with the discontinuity of the water-gas process. The producer process is the simplest type of total gasification of solid fuel.

From the brief description of the fuel bed given there appears the obvious subdivision of the producer fuel bed into four layers: (1) ash bed, supported by a grate; (2) oxidation zone with reaction 1 predominating; (3) reduction zone with reaction 3 predominating; and (4) preheating zone.

The producer described here is the most common type; the fuel moves downward and the gases upward, and it is sometimes called the up-draft type. Later different types of producers such as down-draft, cross-draft, and double-draft producers will be described. Furthermore, gases other than air can be used as blast: air and carbon dioxide, air and oxygen, oxygen, and oxygen with additions. Fuels used in pro-

ducers may include almost pure carbon like charcoal, coke, etc., as well as other carbonaceous material like different types of coal, lignite, wood, and waste materials.

The theory of the producer reactions is of importance in the study of the mechanism of operation of the producer plant in order to find the optimum conditions for the conversion of fuel to gas. These conditions are: (1) highest thermal efficiency; (2) ease of operation; and (3) best quality of gas for the ultimate purpose.

EXPERIMENTAL RESULTS

The early literature on producer theory is given in a book by Wyer [67] containing references from 1840 to 1905. More recent bibliographies are Fernald's [68] and a pamphlet of the British Iron and Steel Institute.[69]

A number of authors have made tests on producers of large and small size, in which temperatures were taken at different levels of the fuel bed as well as gas analyses at corresponding locations. Thus the trend of the reaction in the producer was determined empirically. The results of such work are shown in Fig. 13 derived from the work of Nicholls [70] on a fuel bed of high-temperature coke blown with air of different temperatures. In similar earlier tests by Kreisinger et al.[21] the fuel bed was arranged in a brick-lined, cylindrical shell, 13.5 inches in diameter, and samples were taken every 1.5 inches. The fuel studied was 1 to 1.5 inches in size. The principal conclusions from this representation are:

1. The oxygen is consumed in the first 4 inches above the grate, and the carbon dioxide increased to a maximum of 10 to 16 percent.

2. A maximum temperature of 1,500 to 1,600° C is attained near the point of maximum carbon dioxide concentration, 3 to 5 inches above the grate.

3. Variation in throughput from 20 to 195 pounds per square foot causes little change in the conditions of the oxidation zone.

4. The point at which all oxygen is consumed varies with the nature and size of the fuel, owing to surface, ash, and combustibility.

5. There is a distinct influence of time of contact and temperature on the reduction of carbon dioxide to the monoxide as previously shown by Clement, Adams, and Haskins.[36] A temperature of 1,300° C is required to give adequate carbon dioxide reduction in the few seconds available in producer practice; below 900° the reduction of carbon dioxide becomes negligible.

6. In order to obtain proper carbon dioxide reduction, a fuel bed height of 2 to 3 feet is adequate.

7. The preheat of the blast influences the conditions of the fuel bed.

8. Ash fuses in the upper layers of the oxidation zone and solidifies 2 to 4 inches from the grate.

Papers by Mott and Wheeler [71] dealt with somewhat the same subject as Kreisinger's, with special emphasis on the reactivity of coke. Materially the same conclusions were arrived at, although the work of Mott and Wheeler took advantage of some 20 years of fuel and gas-reaction re-

[67] Wyer, S. S., *Producer Gas and Gas Producers*, Hill Publishing Co., New York and London, 1907, 308 pp.

[68] Fernald, R. H., and Smith, C. D., *U. S. Bur. Mines, Bull.* **13** (1911), 393 pp.

[69] Iron Steel Inst., London, *Bibliographical Series* No. **6** (1938), 72 pp.

[70] Nicholls, P., *U. S. Bur. Mines, Bull.* **378** (1934), 76 pp.

[71] Mott, R. A., and Wheeler, R. V., *Symposium on Solid Fuels*, Am. Chem. Soc. Meeting, Boston, 1939, pp. 95–107; *The Quality of Coke*, Chapman and Hall, London, 1939, 464 pp., especially p. 6.
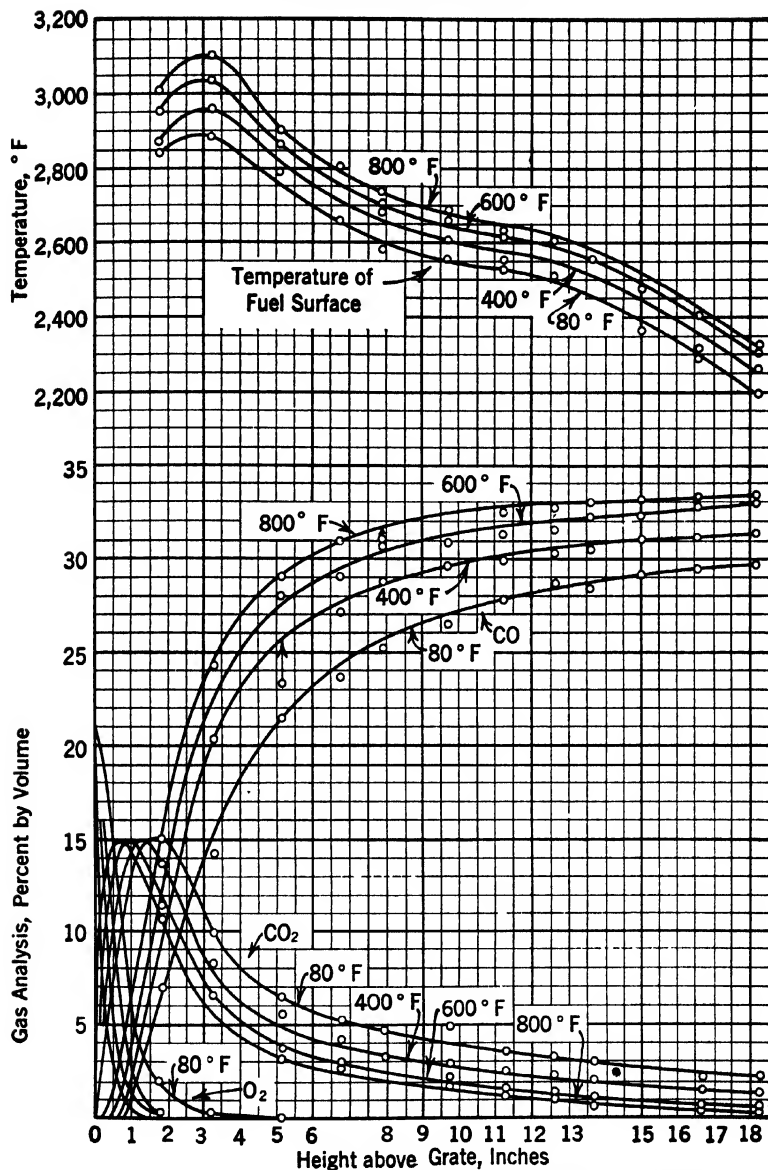
Fig. 13. Effect of preheat on gas analyses and fuel-bed temperatures in an overfeed fuel bed of high-temperature coke.[70]

search. Briefly the conclusions of Mott and Wheeler follow:

At a rate of combustion of 39 pounds per square foot hour, most of the types of coke used consumed all the oxygen in 4 to 6 inches (charcoal in 3 inches) depth of bed. The maximum temperature was 1,560 to 1,800° C, and the highest temperature was attained with the least reactive coke. At the point of disappearance of oxygen the carbon dioxide was at a maximum, or just past it. The maximum temperature was slightly below the point of zero oxygen. The external surface area of the coke pieces (¼ inch or larger) was of more importance than the pore surface. Reactions 1, $C + O_2$, and 3, $CO_2 + C$, were affected in different ways by the conditions of the fuel bed. Above the ignition temperature, reaction 1 depended only on the area of the carbon surface and air supply rate, whereas reaction 3 depended mainly on temperature and secondarily on surface.

In the development of practical producer operations at increasingly fast rates of throughput it became evident that the addition of steam to the air blast was desirable in order to reduce fuel-bed temperatures sufficiently to prevent ash fusion.

With the use of steam, a mixture of $CO + H_2$ is added to the producer gas as well as undecomposed water vapor. The amount of water vapor in the blast generally used varies from 0.4 to 0.7 pound per pound of carbon burned and is decomposed from 60 to 90 percent. The general effects of use of steam are:

1. It cools the fire zone due to the endothermic reactions 6 and 7, hence prevents fusion of ash, cuts down heat losses to walls, and reduces temperature of gas formed; sensible heat of gas is converted into potential heat.

2. Owing to a lowering of fuel-bed temperature with consequent lowering of the rate of reaction 3, the carbon monoxide/carbon dioxide ratio is lowered with increasing steam addition, and hydrogen takes the place of a portion of the monoxide.

3. There is reason to believe that approximate equilibrium according to reaction 8 is established in the gases prior to leaving the fuel bed; reaction 8 is catalyzed by the fuel ash.

4. Excessive steam with incomplete decomposition lowers the thermal efficiency of the producer because of heat carried away in the hot steam vapor.

5. Small amounts of methane are formed in the presence of carbon monoxide and hydrogen.

6. The calorific value of the producer gas is increased by the addition of $CO + H_2$ without accompanying diluent nitrogen gas.

Numerous investigations have been made on the influence of varying steam additions to air blast on producer performance. As pointed out by Denig,[72] however, "the practical operator in the end becomes concerned with only one fact, clinker trouble" and the steam-air ratio is so adjusted as to obtain easy operation.

The work of Neumann[38] is important in being among the first to give data on the oxygen, carbon dioxide, carbon monoxide, hydrogen, methane, water, and nitrogen content of gas and temperatures at different elevations of the fuel bed while using dry air blast as well as additions of steam from 0.38 to 1.82 kilograms per kilogram of carbon burned. Neumann advocated the use of a steam-fuel ratio of 0.4 for optimum gas composition, and a deep fuel bed to complete carbon dioxide reduction as well as possible.

72 Denig, F., *Carbonization Com. Rept., Am. Gas Assoc.*, 1927.

Bone and Wheeler [73] in some earlier work gave an excellent set of data on large-scale results obtained with a Mond producer using coal and steam-fuel ratios of 0.2 to 1.55 with the depth of fuel bed ranging 3.5 to 7 feet.

Seigle [74] calculated the possible heat yields, calorific values, and gas combustion temperatures obtained with producer gas derived from 1 kilogram of solid fuel. He arrived at the conclusion that, when raising the hydrogen content of the gas by increasing the amount of steam in the blast at equal total heat yield, both the calorific value of the gas and the combustion temperature will be lowered. The total number of heat units obtained per kilogram of fuel varied little with increase in hydrogen content of gas. High steam additions cut down clinker formation and with it fuel loss in clinker. Excessive steam reduced thermal efficiency. The work of Seigle is particularly interesting since it is one of the first of a number of stoichiometrical and graphical studies of producer performance.

Haslam and coworkers [20] studied experimentally the reactions in gas producers with air-steam blast using coke or anthracite. The experimental producer was studied with a fuel bed 1.5 to 4.5 feet deep having a firing rate of 10 to 70 pounds of fuel per square foot of grate area per hour. Their work has been outstanding in elucidating the processes constituting the making of up-draft producer gas. Some of their conclusions, especially the predominance of reaction 7 over 6, have been attacked by later authors. It has also been claimed that their results are partly obscured by the use of an experimental producer having too small a cross-sectional area and hence too great a wall effect.

Among the conclusions of Haslam, partly based on correlation of results of previous workers, are the following:

1. The percentage of undecomposed steam, $(H_2O)/(H_2 + H_2O)$, is the controlling factor in the carbon monoxide/carbon dioxide ratio of the gas formed, while the temperature or pressure of the steam has only a minor influence. Figure 5 represents this relationship.

2. The air-steam blast is preheated by the ashes underlying the oxidation zone. Oxygen is consumed within 3 or 4 inches of fuel bed, and carbon dioxide at the same time reaches a maximum and the monoxide begins to appear. It continues to be formed until the gases leave the fuel bed. Water decomposition starts soon after the carbon monoxide reduction and continues vigorously for 12 to 14 inches (Fig. 14), which is called the primary reduction zone. Above this level, water is decomposed by reaction 8 only. In this zone carbon dioxide continues to be reduced and heat exchange from gas to fuel takes place. Above the reduction zones is situated the drying-out and carbonization zone, as well as the gas zone (Fig. 15).

3. Increase in the steam-fuel ratio above 0.4 causes an increase of carbon dioxide and hydrogen, a decrease in the carbon monoxide content of gas, a decrease in heating value, and a decrease in gas temperature. It also causes a reduction in the percentage of steam decomposed, although the actual pounds of steam decomposed per pound of fuel will increase.

4. Increased depth of fuel bed causes an increase in steam decomposition. With a steam-fuel ratio of 0.40 in the blast the amount decomposed was 0.36 pound for a 7-foot fuel bed, and 0.19 pound for a 3.5-

[73] Bone, W. A., and Wheeler, R. V., *J. Iron Steel Inst.* **73**, 126–60 (1907), **78**, 206–33 (1908).

[74] Seigle, J., *Rev. mét.*, **18**, 608–18 (1921).
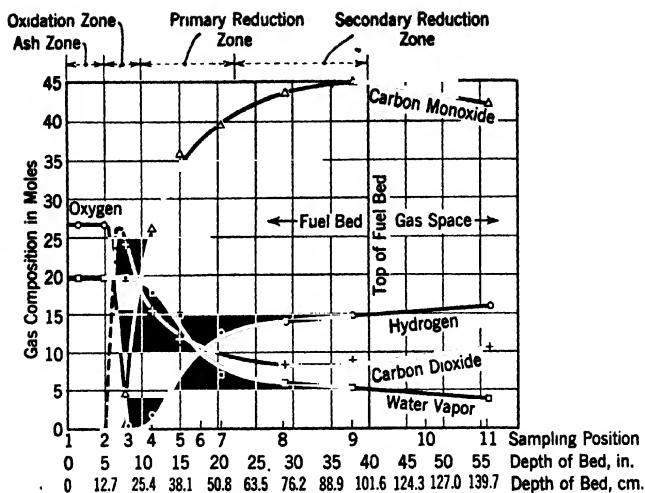
Fig. 14. Composition of gases in the fuel bed of a gas producer. Basis, 100 moles of nitrogen. Fuel used, anthracite or coke, and therefore no distillation zone. After Haslam and Russell.[20]
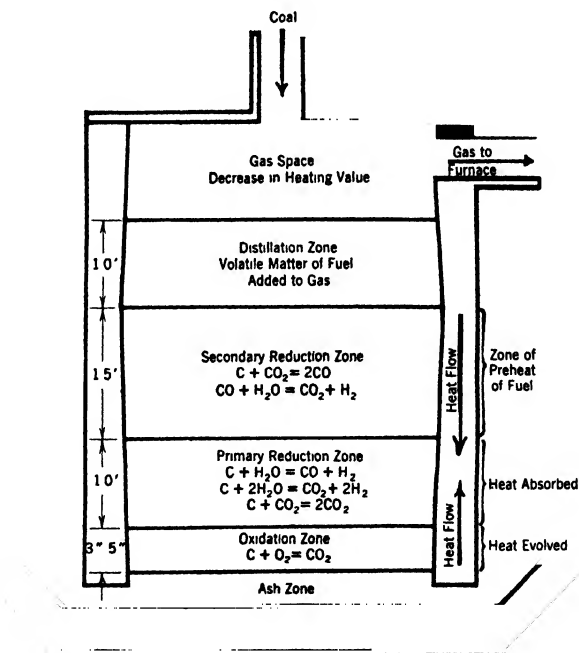
Fig. 15. The reaction zones in the fuel bed of a gas producer. After Haslam and Russell.[20]

foot fuel bed.[73] This increase was attributed principally to a rise in temperature with better rates for reactions 3, 6, and 7 in the reduction zone. The increased temperature was attributed to improved heat exchange in the thicker fuel bed.

5. There is an apparent equilibrium value, K', for $(CO_2) \times (H_2)$: $(H_2O) \times (CO)$ dependent on thickness, L, of fuel bed in feet, and independent of gas velocity (through-put), steam-air ratio, or exit-gas temperature $(K' = 0.096L)$. The values of (CO_2), (H_2), and (CO) were obtained by an Orsat analysis of the dry gas, and (H_2O) was the calculated volume of the total moisture (including that of fuel) per 100 volumes of dry gas. The range of fuel-bed thicknesses covered was 3 to 7 feet. It was claimed that this equation is accurate to ± 10 percent.

6. Although a steam-fuel ratio of 0.4 is best from the point of view of thermal efficiency of producer operation, calorific value of gas, and efficiency of hot gas, an increase of this value to 0.5 or 0.6 is often required to suit the fusion point of coal ash.

7. With high gasification rates (up to 70 pounds per square foot per hour) the maximum temperature in the reduction zone increases. Thus for a 3-foot fuel bed the temperature increased from 1,600 to 2,400° F for 10- to 70-pound rates; the percentage decomposition of steam increased from 67 to 97 percent; and the cold efficiency of the gas rose from 63 to 74 percent.

Large-scale work in a Pintsch producer published by deVoogd[75] is of interest in connection with Haslam's results and Seigle's predictions. DeVoogd claimed that the cold efficiency need not decrease with steam-fuel ratios above 0.4. With higher ratios the hydrogen content will be higher, as well as the carbon dioxide content, and, even if the calorific value of the gas is occasionally lower, the volume of gas made may compensate for this and result in a better cold efficiency. He compared one gas containing 6.5 percent carbon dioxide and having 1,071 calories per cubic meter with a cold efficiency of 80.9 percent to another gas having 4.3 percent carbon dioxide, 1,082 calories per cubic meter, and a cold efficiency of 79.8 percent. It was also pointed out that increased water content of the gas may promote better radiational heat transfer of the gas. Higher throughput was conducive to better efficiency and allowed the use of higher steam ratios. For fuel beds 2 to 4 feet high a steam-fuel ratio of 0.7 was advocated, having a throughput as high as 137 kilograms per square meter per hour (28 pounds per square foot per hour).

An elaborate paper by Terres and Schierenbeck[76] in 1924 dealt with Neumann's work and their own experiments conducted on two types of stationary square brick-shaft coke producers, one with a horizontal grate, and the other with an inclined grate. Their conclusions in the light of present knowledge are perhaps typical for what might be expected with stationary producers. They claimed that equilibrium was attained for reactions 3 and 6, with only secondary effects of reactions 7 and 8 in a fuel bed 60 centimeters (24 inches) thick. Also a reversion of reaction 3 in higher fuel beds was claimed. Optimum gas was obtained with a steam-fuel ratio of 0.5 to 0.6. The ratio between total grate area and shaft area should be high enough to avoid very definite channeling in the fuel bed. In a

[75] DeVoogd, J. G., *Het Gas*, **48**, 214–24 (1928).

[76] Terres, E., and Schierenbeck, J., *Gas- u. Wasserfach*, **67**, 257–63, 279–82, 296–9, 311–4, 325–7 (1924).

later paper, Terres [77] claimed that for a given fuel the efficiency of a producer has a maximum for a certain height and diameter, the diameter being especially significant because of difficulty in the air distribution. Values of 7 percent of carbon dioxide at the walls, and 4.2 percent carbon dioxide in the center were given. Such differences were claimed to be due to cooling of the walls. It is believed that the influence of too many secondary effects confuses the picture of producer reactions in this work, since some of the conclusions were retracted in later work of Terres.[26] Many other papers dealing with the same subject have been published.[78]

GRAPHICAL REPRESENTATIONS

In 1919 Ostwald [79] proposed a method for the graphical representation of the conditions encountered in producer operation utilizing Gibbs' triangular coordinates. It was assumed that carbon is consumed in a producer in three ways:

[77] Terres, E., *ibid.*, **71**, 1205–18 (1928).

[78] Koschmieder, H., *Brennstoff-Chem.*, **2**, 3–5, 25–6 (1921). Laffargue, M., *Chimie & industrie*, Special No., 230–3, May 1924. Husson, G., *Rev. ind. minérale*, **1925**, 451–72. Korevaar, A., *Chem. Weekblad*, **22**, 66–73 (1925). Osann, B., *Stahl u. Eisen*, **45**, 1566–8 (1925). Thibeau, J., *Rev. universelle mines*, **6**, 313–48 (1925), **7**, 25–42, 74–92, 156–68, 186–99 (1925). De la Condamine, C., *Chaleur et ind.*, **7**, 343–50, 402–10 (1926). Goff, J. A., *Ind. Eng. Chem.*, **18**, 585–8 (1926). Gwosdz, J., *Feuerungstech.*, **15**, 37–9, 52–5, 63–7 (1926) ; *Brennstoff- u. Wärmewirt.*, **11**, 229–32, 251–4 (1929). Guillon, H., *Chaleur et ind.*, **9**, 581–7 (1928), **10**, 37–43 (1929), **11**, 298–303 (1930). Romlg, J. W., *Am. Gas J.*, **133**, No. 1, 47–9, No. 2, 47–8, No. 3, 44–5, No. 4, 68, 73–4, No. 6, 45–6, 59 (1930), **134**, No. 1, 54–5 (1931). Lehmann, R., *Glashütte*, **63**, 270 (1933). Wohlschläger, H., *Feuerungstech.*, **26**, 102–6 (1938). Müller, W. J., and Graf, E., *Brennstoff-Chem.*, **20**, 241–6 (1939).

[79] Ostwald, Wa., *Chem.-Ztg.*, **43**, 229–31 (1919) ; *Stahl u. Eisen*, **39**, 625–6 (1919) ; *Feuerungstech.*, **21**, 81–4 (1933) ; *Beiträge zur graphischen Feuerungstechnik*, O. Spamer, Leipzig, 1920, 85 pp.

(1) $a (C + O_2)$

$$= a\, CO_2 + a\,(94{,}390) \text{ calories}$$

(7) $b (C + 2H_2O) = b\, CO_2$

$$+ b\, 2H_2 - b\,(21{,}270) \text{ calories}$$

(3) $c (C + CO_2)$

$$= c\, 2CO - c\,(41{,}410) \text{ calories}$$

It follows that each point in a triangular coordinate system with coordinates a, b, and c can be made to represent a condition in which the respective fractions a, b, and c of 1 mole carbon are gasified according to the above equations. Figure 16 represents such a triangle in which the corners A, B, and C represent complete reactions according to 1, 7, or 3: A represents complete combustion of carbon with oxygen to carbon dioxide and is called the combustion angle; B represents completion of reaction 7 in the water-gas angle; and C is the reduction angle. Other possible reactions are represented by points in the triangle: e.g., $C + H_2O = CO + H_2$ is halfway between B and C.

It is a simple stoichiometric problem to locate the operating conditions of a producer in the diagram if the gas analysis is given:

$$a = \frac{2CO_2 + CO - N_2}{2}\, x$$

$$b = \frac{H_2}{2}\, x$$

$$c = \frac{CO}{2}\, x$$

with $a + b + c = 100$.

The portion DCE of the triangle is generally unused; it requires carbon dioxide addition from other sources than the carbon present. The line FG is the so-called *neutro calore*; to the right of it external heat must be supplied, points on FG rep-

resent conditions of operation with zero overall heat effect. Hence the "gas trapezium" *ADFG* includes all practical conditions of operation.

Dawidowski [80] has given an analysis of the Ostwald triangle and included methods for the calculation of points if volatile matter (coal) is present, still further limiting the useful area of the triangle to the hexagon *KLMNOP*.
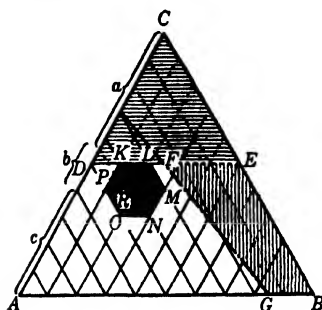
Fig. 16. Gasification trapezium and hexagon.[80]

Dolinski [81] enlarged the representation for better visibility and included sets of parallel lines for hydrogen, carbon monoxide, nitrogen, carbon dioxide, and oxygen percentages as well as for the heating values. The importance of gas analysis as related to factors concerning producer operation such as steam-fuel ratio and depth of charge was discussed in some detail. Definite trends of the representative points were observed for each type of change. Furthermore the graph could be used to predict gas analyses from the saturation temperature of blast and carbon dioxide content of gas and also for a check upon the actual gas analysis.

From the viewpoint of rapid interpretation of gas-analysis results the graphical

method has some evident merit. It has one drawback in common with all other stoichiometric "theories" in that it offers no deeper insight to the process than is already inherent in the plain reaction equations. Several other authors [82] have contributed to the discussions of the Ostwald graphical method.

Seigle [74] used a somewhat different method in developing his conclusions based upon stoichiometrical results. He represented the gas analyses in a three-dimensional system having carbon dioxide, carbon monoxide, and hydrogen axes. Application of the triangular coordinates to the manufacture of synthesis gas has also been given by Dolch.[83] Recently a new type of graphical representation has been worked out by Fehling.[84] It is based on the two principal stoichiometric relationships with

A moles of O_2 reacting to give CO_2

$1 - A$ moles of O_2 reacting to give CO

S moles of steam reacting to give H_2, CO (or CO_2)

S^1 moles of steam remaining undecomposed

The variables are *A*, *S*, and S^1. From these can be determined by latent- and sensible-heat calculations the temperature *t*, or the calorific value *C*, of the gas formed. A further relation between *A*, *S*, and S^1 was derived from the equilibrium constants, preferably those of the water-gas reaction.

80 Dawidowski, R., *Fcuerungstech.*, **25**, 183–95 (1937); *Fuel*, **17**, 166–71, 210–7 (1938).

81 Dolinski, J., *Przemysl Chem.*, **11**, 757–63 (1927).

82 Griepe, A. W. H., *Am. Gas J.*, **116**, 435–9, 446–7 (1922). Ruhland, M., *Gas- u. Wasserfach*, **70**, 642–6, 664–7, 688–92, 712–6 (1927). Schulze-Manitius, H., *Feuerungstech.*, **21**, 65–71 (1933). Schwarz von Bergkampf, E., *Z. Elektrochem.*, **43**, 636–8 (1937).

83 Dolch, P., *Feuerungstech.*, **27**, 1–5, 44–51 (1939).

84 Fehling, H. R., *J. Inst. Fuel*, **14**, 39–46 (1940).

Thus three equations, schematically represented by

$$C = F_1 (A, S, S^1) \qquad (I)$$

$$t = F_2 (A, S, S^1) \qquad (II)$$

$$t = F_3 (A, S, S^1) \text{ from } K_8 = F(t) \qquad (III)$$

are available. By eliminating one variable between II and III, there is opened the possibility of representing the gas condition at any point in the producer by two variables. The net result was expressed in a graph (Fig. 17) with the steam addition per pound of carbon as abscissa, the gas temperature as ordinate. The possible

conditions in the diagram are delimited by an upper line of complete combustion, no steam decomposition, and a lower line of complete steam decomposition. Lines of constant decomposition from 0 to 100 percent and of constant calorific value fill up the space between upper and lower boundaries in the diagram. The most interesting lines running diagonally are those of equal air saturation temperature. They include (going from top to bottom) the temperature and calorific values of a gas entering with a given air saturation temperature on its way up through the fuel bed (reaction lines).
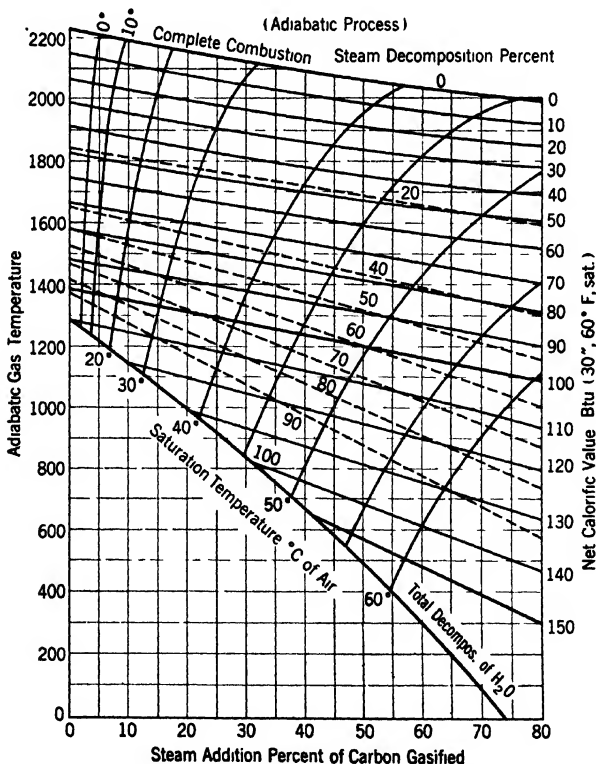
Fig. 17. Equilibrium diagram for an adiabatic gasification process.[34]

All the results obtained in the discussion of this graph naturally apply only for gas in a state of equilibrium, and the reaction line will terminate at a point above the line of complete steam decomposition due to lack of temperature for equilibrium establishment. Up to 45° C saturation temperature, the agreement of the graphical results with Neumann's tests is striking; above 45° C saturation, the equilibrium state (depending on temperature and fuel reactivity) is seldom reached. The author proposed the term "thermodynamic efficiency" of the producer for the degree of attainment of the thermodynamic equilibrium. For air gas producers, the thermodynamic efficiency may be as high as 95 percent with only 60 percent thermal efficiency. This work has certain features in common with that of Cerasoli [85] and of Coste.[86]

STOICHIOMETRY

A considerable part of the literature concerned with the producer process consists of calculation and recalculation of the basic equations of the various reactions involved.

Seigle [74, 87] has shown that, for a gas having a percentage composition of $a N_2$, $c CO_2$, $d CO$, $e H_2$, $f H_2O$ vapor, it follows from oxygen, nitrogen, and hydrogen balances that

$$4.76\,c + 2.88\,d - 0.88\,e + f = 100$$

Furthermore, for a gas volume of U cubic meter (0°, 760 millimeters) per kilogram carbon

$$U = \frac{186}{c + d}$$

and the amount, W in kilograms, of steam per kilogram carbon gasified is determined from the expression

[85] Cerasoli, T., *Gas- u. Wasserfach*, **70**, 508–10 (1927).

[86] Coste, P., *Rev. mét.*, **32**, 225–9 (1935).

[87] Seigle, J., *Bull. soc. ind. minérale*, **14**, 79–108 (1918); *Rev. mét.*, **18**, 81–91 (1921).

$$W = 186\,\frac{e + f}{c + d}$$

If c', d', e' are the contents of carbon dioxide, carbon monoxide, and hydrogen, respectively, of the gas determined by ordinary gas analysis, i.e., after condensation of the excess steam, then

$$4.76\,c' + 2.88\,d' - 0.88\,e' = 100$$

This simple but useful relationship served as the basis of a graphical method correlating the various factors influencing gas production. However, from it a few far-fetched conclusions were obtained, some of which have been previously cited.

German methods of calculation have been discussed by Brodmann and Schrader.[88]

Walker [89] has treated gasification reactions in a general manner involving the concept of a combustible agent having a composition $C_x H_y O_z$ which is converted either to $CO + H_2$ directly or to $CO_2 + H_2O$ with a subsequent reduction to $CO + H_2$. Steam as well as exhaust gases were considered as endothermic agents in the producer reaction. All operating factors and resulting products were calculated for 100 percent producer efficiency, and tabulations were given for different fuels by varying x, y, and z. In addition to these formal calculations Walker presented data obtained by Swardt operating a "National" gas producer and engine with charcoal and exhaust gases as the endothermic agent instead of steam. The conclusions arrived at from the calculations were principally that the use of exhaust gases instead of steam reduces the calorific value of the producer gas but tends to produce larger volumes of gas of a higher density. The idea of injecting liquid fuel into a producer was con-

[88] Brodmann, L., and Schrader, H., *Arch. Eisenhüttenw.*, **3**, 133–8 (1929).

[89] Walker, W. J., *Trans. Inst. Chem. Engrs.*, *London*, **13**, 121–30 (1935).

sidered in the paper. A similar discussion was given by Segal.[90]

Another typical paper on stoichiometry and graphical representation of producer data is that of Koelsch.[91] His general equation for the ideal producer reaction is expressed by the following:

$$C + L \times O_2 + D \times H_2O$$
$$= (2 - 2L - D)\ CO$$
$$+ (2L + D - 1)\ CO_2 + DH_2$$
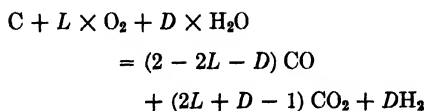
in which $L = x_1$, the fraction of C consumed by the reaction $C + O_2 = CO_2$; and $D = 2x_2$, the fraction of C required in the reaction $C + 2H_2O = CO_2 + 2H_2$.

The above equation was used as a basis for triangular coordinates, and the usual typical lines and points were worked out in great detail. In addition methane was included in the discussions. It is obvious that such work is doomed to be extremely limited in scope and cannot go beyond the interpretation of operating results.

MISCELLANEOUS THEORIES

About 1924 a set of interesting papers and a book on producer theory were published by Korevaar.[66, 92] Their somewhat controversial nature had a stimulating effect on work undertaken in later years.

Korevaar, basing his concepts on Le Châtelier's earlier work,[66] assumed that a producer is a shell filled with a column of carbon composed of uniformly distributed pieces. The entire zone of combustion (oxidation and reduction layers) of carbon to carbon monoxide as a whole was assumed to be at a uniform temperature.

[90] Segal, B., *J. S. African Inst. Engrs.*, **35**, 204–9 (1937).

[91] Koelsch, H., *Feuerungstech.*, **27**, 195–201 (1939).

[92] Korevaar, A., *Chimie & industrie*, **8**, 12–15 (1922); *Stahl u. Eisen*, **43**, 481–5 (1923); *Chem. Weekblad*, **22**, 280–5 (1925).

The carbon surface reacted with oxygen from the air at a rate determined by the nature of carbon (activity), temperature, and oxygen concentrations. At a given air rate of x kilogram per minute and with sufficient carbon to fill the space, the zone of combustion then has a definite height and volume V. The air entered the lower limiting plane of this volume, and the finished gas product left at the upper plane, the temperature of the entire zone being T. Heat was evolved in this zone of combustion only. The activity of the carbon was expressed as y kilogram of air used per minute per unit of surface area. Factors influencing the temperature and volume of the combustion zone were: (a) furnace factors—size of producer, mode of construction, and type of construction materials; (b) air factors—velocity, temperature, moisture and oxygen of the air; and (c) carbon factors—activity, porosity, size, and ash content. In discussing the carbon factors Korevaar pointed out that a high intrinsic carbon activity tends to accelerate all the reactions involved, hence a smaller combustion zone volume is required. High porosity, similarly small particle size (large surface area per unit weight), and low ash content (diluent) have the same net effect.

Assuming that the heat introduced by the air is A, the heat liberated from carbon combustion is B, the heat introduced by preheated carbon entering from above the combustion zone is C, the heat removed by the evolved gases is D, neglecting ash, there is left per minute in the combustion zone an amount of heat

$$A + B + C - D = a$$

and since it maintains a steady state condition, where F is the heat loss,

$$a = F$$

The hot gases traversing the combustion zone lose heat by conductivity and radiation, and it was assumed that the gas and carbon were more or less at the same temperature. Evaluating the various factors involved in the heat balance, the following expression for the steady state of dynamic equilibrium in the producer was obtained:

$$O = \frac{x(407 + 0.24t - 0.265T)}{K(T - T_0)}$$

where O is the surface of the cylindrical wall surrounding the combustion zone; x, the kilogram air blast per minute; t, the air temperature; T, the combustion zone temperature; T_0, the temperature of the surrounding wall; and K, the heat transfer coefficient of the gas to the wall. From this equation one readily observes that, for constant x and t, O becomes smaller for increasing T, which results from variation in the carbon activity. This was called the "law" of heat compression. Burning carbon in a gas producer with constant air factors, hence constant fuel consumption, it follows that a higher temperature can be obtained in a smaller volume by using more active carbon, more porous carbon, smaller-sized carbon, or carbon with less ash.

In developing further the kinetics of his theory, Korevaar obtained a curve for the oxygen and carbon dioxide content of the gases along the vertical axis of the producer. With lower temperatures in the combustion zone and larger volumes, the carbon dioxide content of the gas eventually increased; normally the combustion zone was smaller than the actual carbon column and the carbon column had to be varied according to the combustion zone. With too high a carbon column, again a slight increase in carbon dioxide content of the gases resulted from the reversion of reaction 3. Different cases were discussed in which the total height of carbon column was less than the combustion zone. This resulted in incomplete carbon dioxide reduction. A new explanation was derived for the results of the experiments of Koppers [93] with furnaces in which cokes of different activity were used, and the essential features of cupola operation could be explained upon this basis.

If the air factor is varied (air rate x raised), it is difficult to predict from the basic equation whether O should increase or decrease. Increasing x tends to raise T, thereby compensating the direct effect of x upon O. There is, however, a maximum value for T depending upon the combustibility of the carbon, and above this T_{max} increasing x will, of course, cause expansion of the combustion zone. As to the air temperature t, its effect is the same as that of increased carbon activity. Increasing t causes O to decrease to a minimum while T tends to increase. Water vapor in the air enlarges the combustion zone. The furnace factors K and the diameter D affect the heat zone in such a manner that, for a constant height and constant air rate, the temperature T increases with increasing D or decreasing K.

A number of commonly known effects were explained by Korevaar. Preheated blast in high shaft producers results in lower top temperatures owing to the decreased height of combustion zone, which in turn increases the height of the superimposed heat-exchange zone. With sufficient basic data the equation for O may be used for producer design.

Korevaar's work is open to criticism on several grounds, primarily because pertinent theoretical data were lacking or not realized at the time of his work. A few con-

93 Koppers, H., *Stahl u. Eisen*, **42**, 569–73 (1922).

troversial issues brought forth by more recent work are: (1) as temperature plays a role only in the reduction zone, the effect of the air rate is confused; (2) more recent work shows a contraction of hot zone with increased air rate; and (3) at the temperatures prevailing in the larger part of the combustion zone, differences in the activity of the carbon species are not pronounced. Even if more recent work has superseded Korevaar's conclusions in some respects his conception of a fuel bed has very distinct merits. It should also be kept in mind that several questions raised by Korevaar are as yet unsolved.

An interesting study of producer reactions has been published by Walker, Lewis, McAdams, and Gilliland [94] in an effort to build up a quantitative relationship among the three principal factors of a producer, blast rate, height of fuel bed, and steam ratio in blast. Noting that for reactions 3, $C + CO_2$, 6, $C + H_2O$, and 7, $C + 2H_2O$, the reaction-rate constants K_3, K_6, and K_7 remain in about the same ratio between 1,000 and 1,200° C, there was derived from Haslam's work the relation

$$1.01v = x + (26.9 - x_0)\left(\frac{x}{x_0}\right)^{1.319}$$

in which v is the carbon monoxide content

$H_2O = CO_2 + H_2$, after other reactions have stopped. It was claimed that for coke producers the calculated carbon dioxide values agreed with experimental values. For coal producer gas the actual carbon dioxide values were 3.6 units higher, and a modified equation was proposed for correction. Figure 18 depicts the relationship between the undecomposed steam and the v value doubly corrected. Surprisingly, a similar set of curves will follow from the assumption that the composition of gas leaving the fuel bed follows the equilibrium of reaction 8 at 2,000° F with $K_p = 2$. These curves enable an·operator to check his analysis with what should be expected for known values of x and x_0. Conversely, for a known gas analysis, it is possible to predict the values for x and x_0.

The further study of the producer process by these authors was based upon the following concepts. It was assumed that 100 moles of nitrogen enter a producer with 26.6 moles of oxygen and burn to carbon dioxide in the oxidation zone. At some level in the reducing zone at temperature t, the heat current flowing upward consists of three principal quantities summarized by the expression

$$\frac{Q}{A\theta} = r\,[2,580,000 - (920 + 9x_0)(t - t_a) - 34,000_{g0} - z)]\quad \text{(heats in Chu, } t \text{ in °C)}$$

of the gas, x the undecomposed steam of the gas, and x_0 the steam used in the blast, all calculated as parts per 100 parts of nitrogen.

Carbon dioxide values calculated from x and x_0 are often low as the result of the Neumann reversal reaction of $CO = CO_2 + C$ and continuation of reaction 8, $CO +$

94 Walker, W. H., Lewis, W. K., McAdams, W. H., and Gilliland, E. R., *Principles of Chemical Engineering*, McGraw-Hill Book Co., New York, 1937, 749 pp.

in which Q is the amount of heat (Chu); θ, the time in hours; A, the area in square feet; r, the number of moles of nitrogen rising per hour per square foot divided by 100; x_0, the moles of steam entering with the air; t_a, the temperature of the materials entering the producer; z_0, the total moles of initial carbon dioxide + steam; and z, the unreduced portion of carbon dioxide + steam.

The first term, 2,580,000, represents the heat of combustion of carbon with 26.6
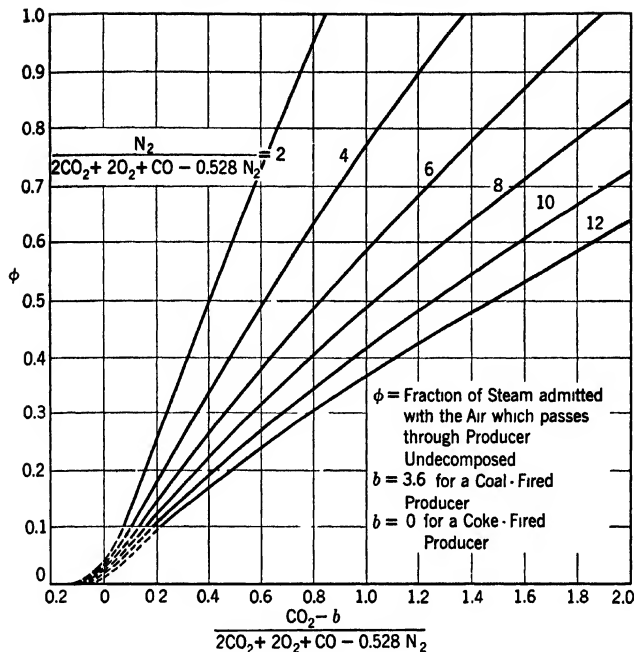
Fig. 18. Steam decomposition in gas producers.[54]

moles of oxygen; the second term, $(920 + 9x_0)$ $(t - t_a)$, includes the specific heats of nitrogen + carbon dioxide − carbon $(740 + 305 - 125)$ plus steam $(9x_0)$ times the temperature above the datum level; the third term in the equation represents the heat consumed by carbon dioxide and water reduction below the level under consideration. This term is equal to $34,000$ times the portion of the carbon dioxide and water reduced.

Introducing the thermal conductivity a by means of the expression

$$\frac{Q}{A\theta} = -a\,\frac{dt}{dL}$$

where L is the vertical dimension, and the reaction rate r by

$$r\,\frac{dz}{dL} = -Kz e^b$$

the above equation was integrated after some approximation to

$$e^{bt_0} = Kr^2\left[B\ln\frac{z_0}{z_1} + 34,000(z_0 - z_1)\right]$$

In this equation, b is $0.006 - 0.007$, K is a constant depending on the type of fuel used, and B is $2,580,000 - (920 + 9x_0)\left(\dfrac{t_0 + t_1}{2} - t_a\right)$ $- 34,000z_0$. The subscripts 0 and 1 in the equation refer to the conditions at the bottom and the top of the reducing zone respectively.

Qualitative interpretation of these equations by the authors resulted in the following conclusions:

1. The rate of operation r increases as the square root of the exponential function of the left-hand side, i.e., not as rapidly as would follow for the increase in reaction rates based on temperature of the oxidation zone alone.

2. With an increase in temperature, both rate and steam and carbon dioxide decomposition (first power) improve and therefore the steam rate may be increased if desired.

3. The value of $z_0 - z$, representing moles $CO_2 + H_2O$ reduced per 100 mole N_2, is found surprisingly constant (for cold air-steam it is about 30), the value decreasing slightly with increasing steam-air ratio and increasing with preheating of the blast. At 250° C blast temperature Bone and Wheeler obtained a value of 42, at 80° C Haslam found 31, both in fair agreement with values calculated from the above equations. Approximately, the reduction obtained in a producer, if the full bed is of adequate depth, is expressed by

$$z_0 - z_1 = 54 - 0.04x_0 - 0.018(t_1 - t_a)$$

where temperature is expressed in Fahrenheit degrees. Generally the value of t_1 will vary with the depth of fuel bed from 1,100 to 1,500° F. The computation method of Walker and coworkers is so far the most instructive one and amplifies the work of Korevaar in a quantitative manner.

For producers operating with solid-ash-removal systems, it is evident that the benefits of increased temperature of oxidation zone are only limited by the necessity of keeping the ash from fusing into large blocks of clinker. Rather than allowing a temperature rise to occur at increased rates, it is found most practical to increase the steam-air ratio.

One statement made by the same authors, that best operating conditions are obtained with a relatively thin fuel bed run at slow rate,[95] is somewhat questionable in the light of their own theories.

Among other work dealing with predictions of producer reaction may be mentioned that of Laffargue[78] and that of Coste.[86] In a brief thermodynamic study Coste calculated the equilibrium conditions to be expected for various steam-air ratios at different temperatures. This type of calculation (see also Cerasoli for water gas) is limited in its usefulness because actually equilibria are hardly ever attained.[96]

Paquay[97] has discussed the different thermodynamic features and their practical application to the producer process. He set forth a theory of producer reactions in which the beneficial effect of high blast rates was especially stressed. High blast rates result in a concentration of heat at the boundary line between oxidation and reduction zone, since heat loss away from the producer is relatively less as well as heat transmission from this boundary to the other parts of the fuel bed. As a result the temperature at the boundary increases to 1,200° C or more to give extremely rapid reduction of carbon dioxide as exemplified in the Gohin producer and in the blast furnace. Another advantage of the rapid blowing rate is relatively less opportunity for the carbon monoxide to carbon dioxide dissociation to occur. It was pointed out that ash fusion takes place principally at the boundary line between oxidation and reduction zone.

Thring[98] has discussed fuel-bed conditions and considered temperature, gas velocity, particle size, and fuel reactivity as the four principal factors in the producer

[95] See p. 227 of ref. 94.

[96] Cf. ref. 84.

[97] Paquay, H., *Chaleur et ind.*, **20**, 263–70, 316–22 (1939).

[98] Thring, M. W., *J. Inst. Fuel*, **14**, 47–62 (1940).

process. Unpublished curves of L. H. F. Nicholls on the change of carbon dioxide reduction rate in the fuel bed with temperature indicated a 1.5 to 2 fold increase in rate with each 100° C rise. The outstanding primary effect of temperature on the reduction process (even if this is no longer the only means of carbon monoxide formation) is thus evident. Gas velocity was shown to be principally effective through its effect on temperature: higher gas velocity means relatively less heat loss through the walls, hence higher bed temperature. The effect of heat loss from a fuel bed was found to be especially large at that point in the bed where the carbon dioxide content is at a maximum, indicating that a large part of the energy of the gas is carried as sensible heat.

SUMMARY OF CONVENTIONAL PRODUCER PRACTICE AND ITS VARIATIONS

All the work dealt with up to this point is concerned with what might be called the conventional theory of producer operation. Briefly the outcome of the investigations can be summarized as follows:

A simple up-draft producer is operated with a carbonaceous fuel and cold air blast to which usually steam is added. The purpose of steam additions is (1) to reduce the temperature of the combustion zone in order to regulate the size of the ash particles and to reduce heat losses; (2) to increase the "cold" efficiency of the producer by converting more of the sensible heat of the gases produced into available heat of combustion of the gas; and (3) to modify the burning characteristics of the gas. Excessive steam is detrimental to efficiency because of excessive cooling of the fuel bed and increased sensible heat carried away by the undecomposed steam. The practical optimum for operations requires from 0.4 to 0.7 pound of steam per pound of fuel, depending upon the rate of operation of the producer.

Among the variables affecting the thermal yield of a producer operating with a given fuel, two factors are outstanding: (1) the rate of firing; and (2) the height of the fuel bed. These operational factors influence directly the height and temperature of the reduction zone and consequently the extent to which carbon dioxide and water are reduced, which, in turn, determines the portion of sensible heat converted to chemical energy in the gases produced. Generally an increase in the rate of firing tends to increase the temperature of the combustion zone but does not affect its height. For the same height, increased rates of firing permit the use of additional steam in the blast. Increased height of fuel bed improves the heat exchange between fresh fuel and gases, thereby raising the temperature of the reduction zone. Depending on fuel size and combustibility, there is generally a minimum height of fuel bed necessary to insure the maximum reduction. The temperature at the top of the fuel bed should be below that required for carbon dioxide and water reduction. The allowable temperature of the fuel bed depends on the fusion point of the fuel ash and in normal practice ranges from 1,800 to 2,800° F while the minimum height of fuel bed ranges from 2 to 6 feet for the majority of fuels in common use.

In the foregoing discussion, it was assumed that the fuel bed was maintained in a uniform condition, and that the boundaries of the various zones were as nearly as possible horizontal. This precludes the presence of "blow holes" through which oxygen or carbon dioxide bypasses all or part of the fuel bed. With the exception of minor details there is a fair agreement on all the above points in the conventional producer reaction mechanism.

It might be pointed out, however, that to date no final satisfactory quantitative theory of the producer mechanism exists. Such a theory requires complete knowledge of the kinetics of the individual reactions involved and of the physical phenomena occurring. The existing knowledge of the former has been discussed in a previous chapter; knowledge of the latter, including factors such as aerodynamics of gases in beds of fuel and heat transfer between gases and solids, is as yet incomplete. Efforts to calculate the reactions in fuel beds similar to those made by Mayers [99] deserve extension to producer conditions. Specific comments pertaining to this subject have been made by Gumz.[100] A paper containing some forty-four references by Rosin [101] dealing with the aerodynamics in fuel beds is of especial interest in this respect. An initial effort to such a calculation is contained in a paper by Thring [98] The aerodynamics of the fuel bed of portable producers has been studied by Bennett and Brown.[102]

The foregoing brief summary has conformed to the conventional theory, assuming more or less separate oxidation and reduction zones with primary carbon dioxide formation. A large portion of this conventional theory may have to be radically revised. An acceptable producer theory calls for a simultaneous primary production of carbon monoxide and carbon dioxide, the secondary reduction of the dioxide being a process of lesser significance. Original exponents of this newer theory are several Russians, and arguments in favor of this theory are now also being gathered from the work of previous authors. The "single-zone" theory requires the primary monoxide formation to a smaller or larger extent chiefly dependent upon the rate of gas flow past the fuel particles. Grodzovskii and coworkers [18] have proposed it, and Karzhavina [19] has given additional experimental support. The principal reason for its belated appearance may be attributed to the difficulties arising in sampling gases from hot fuel beds, a factor which frequently in the past has prevented detection of the simultaneous presence of carbon monoxide and oxygen, owing to their reaction in the sampling tube. High-speed gasification in vehicle producers has given further impetus to this development. Bangham and Bennett [103] have published a brief review of the old and new theories in which they set forth two significant factors explicable on the basis of the single-zone theory. The two factors are: (1) measured temperatures in the "oxidation zone" are never as high as would be expected from the complete oxidation of carbon to carbon dioxide, nor is the drop in temperature in the reduction zone as abrupt as would follow from the reverse endothermic reaction 3; and (2) fuel consumption takes place only in the first few centimeters of the fuel bed with high-speed producers.

The single-zone theory is as yet in its infancy, and the proper compromise between conventional and new theory requires additional study. Gwosdz [104] has discussed the combustion in vehicle producers along conventional lines. He did not concede primary carbon monoxide formation.

The efficiency and capacity of the up-

99 Mayers, M. A., *Trans. Am. Soc. Mech. Engrs.*, **59**, 279–85 (1937).

100 Gumz, W., *Feuerungstech.*, **27**, 97–9 (1939).

101 Rosin, P. O., *J. Inst. Fuel*, **11**, 26–41 (1937).

102 Bennett, J. G., and Brown, R. L., *Gas J.*, **232**, 378, 383–6 (1940) ; *J. Inst. Fuel*, **13**, 232–46 (1940).

103 Bangham, D. H., and Bennett, J. G., *Fuel*, **19**, 95–101 (1940).

104 Gwosdz, J., *Brennstoff-Chem.*, **21**, 145–51, 269–73 (1940).

draft type of producer is limited by the following requirements: (1) the discharge of solid ash, which in turn limits the temperature of the fuel bed; (2) the use of air with 79 percent inert nitrogen as the oxygen carrier; (3) the height of the fuel bed, which determines the back pressure to the blast and affects the power requirements for a given producer; and (4) the rate of reduction of carbon dioxide and water using the customary fuels. It is obvious that one or several of these requirements must be eliminated if the capacity or efficiency is to be increased. Such modifications of producer characteristics may be subdivided into fuel changes, blast changes, or design changes. Among the possible variations of the fuel that are of interest are the addition of catalysts to the fuel and the use of highly combustible fuels, finely divided fuels, or underground fuel beds *in situ.* Blast changes include the use of air with more than 21 percent oxygen or of pure oxygen, or preheated blast gases, high-velocity blast injections, and the addition of carbon dioxide instead of water to the blast. Design changes include heat insulation of the fuel bed and removal of ash in liquid form.

A number of the above-mentioned changes have been made in producers and related equipment utilized for complete gasification. In several instances, their operation and design extend beyond the boundaries of the available theory, and these developments justify a brief discussion. In this manner deficiencies of the existing theoretical knowledge may be brought to light.

Other developments in producer design and operation that are of theoretical interest are those intended to adapt the principle of total gasification to special fuels, resulting in their most efficient utilization. Examples of such developments are the down-draft producer suitable for coals with high-volatile-matter contents, and the Mond producer with byproduct recovery from the gasification of coal.

PRODUCER OPERATION

USE OF OXYGEN IN PRODUCER BLAST

The addition of oxygen to the air used for producer-gas manufacture or the substitution of oxygen for the air has obvious advantages. These have long been realized, but economic limitations have prevented the use of oxygen from becoming common practice.

With air blast alone, perfect gas production (air gas) will correspond to the completion of the reaction $C + \frac{1}{2}O_2 = CO$, the maximum possible cold efficiency being the ratio 67,900/94,390 or 72 percent. The remaining 28 percent of the heat of combustion of carbon is lost partly as radiation and partly as heat carried away by the hot gases. An average value for the radiation loss is about 5 percent, for the sensible heat carried away by the gases about 23 percent of available heat, corresponding to a temperature of about 1,900° F for the gases leaving the producer. The approximate composition of the gas produced is 35 percent carbon monoxide and 65 percent nitrogen, gross heating value 111 Btu per cubic foot (at 60° F, 30 inches of mercury, saturated). When a proper amount of steam is added to the air blast the heat balance is slightly shifted. The radiation loss remains approximately the same; the sensible heat carried away by the gas is reduced to about 13 percent; the cold efficiency is raised to 82 percent; and the outlet gas temperature is reduced to 1,200° F. The gross heating value of this gas is about 130 Btu per cubic foot.

The substitution of oxygen for air changes the picture. For operation with-

out steam the maximum possible cold efficiency remains unchanged, and the gas made under perfect conditions is 100 percent carbon monoxide, having a gross heating value of 317 Btu per cubic foot. Depending on radiation losses which may be higher on account of higher operating temperatures, the gas temperature will increase to approximately 2,500° F.

For operation with steam, the cold efficiency with the optimum amount of steam increases. Assuming the radiation heat loss to be 5 percent of the heat available in the fuel, and the temperature of gases 1,200° F, the cold efficiency is 88 percent. The sensible heat carried away in the gas is 7 percent; the gas composition is 75 percent carbon monoxide and 25 percent hydrogen, which has a gross heating value of 317 Btu per cubic foot. The above quantities are "perfect" values and are based on the assumption that all carbon dioxide is reduced to the monoxide, and all water to hydrogen. It remains to be seen to what extent these values can actually be realized.

Few developments in producer operation have been discussed in years past with more optimism than oxygen blast. High oxygen content of the blast when used in an ordinary up-draft type producer provided with solid-ash-removal mechanism tends to raise the fire temperature. Hence more steam has to be used per unit of fuel to maintain the fuel-bed temperature below the ash-fusion point. Whereas the above ideal figure includes a balanced condition of the heat effects at 0.5 pound of steam per pound of carbon, the actual amount required may be twice as high. As a result the amount of carbon dioxide and undecomposed steam in the final gas will be appreciable. On the other hand, the relative conditions in the reduction zone will be more favorable than in air-steam operation. The temperature of the reduc-

tion zone will be higher because of better heat exchange between gas and fuel, tending to make the reduction equilibrium more complete. The height of the reduction zone will tend to be less, again improving heat exchange in the upper layers. An unfavorable factor appearing in operations without inert nitrogen is the increased carbon dioxide partial pressure of the gases entering the reduction zone. Owing to the expansion in volume from the reaction $CO_2 + C = 2CO$ there is a tendency for the reaction equilibrium to be displaced towards the carbon dioxide side at higher carbon dioxide pressures. This effect is to some extent counteracted by the increased temperature effect which promotes more complete reduction.

Among the earlier advocates of oxygen blast in producers are Hodsman and Cobb,[105] as well as Jefferies [106] and Willien.[107] Some preliminary work has also appeared in a report of the U. S. Bureau of Mines.[108] In later years, the oxygen gasification was tested out with indifferent results by VandaVeer and Parr.[109] A semicommercial installation for oxygen gasification, described by Frey,[110] was operated for some time at Worcester, Mass. Other test work at Schenectady was reported by Knowlton.[111] Evidently mechanical difficulties discouraged further pursuit of this work.

[105] Hodsman, H. J., and Cobb, J. W., *Trans. Inst. Gas Engrs.*, **18,** 431–52 (1919–20) ; *Gas J.,* **150,** 640–7 (1920). Hodsman, H. J., *Gas World,* **72,** 492–502 (1920) ; *Gas J.,* **153,** 92 (1921).

[106] Jefferies. E. A. W., *Gas Age*, **47,** 145–50 (1921) ; *Gas Record,* **19,** 45–55 (1921).

[107] Willien, L. J., *Proc. Am. Gas Assoc.,* **1923,** 969–74.

[108] Davis, F. W., *U. S. Bur. Mines, Repts. Investigations* **2502** (1923), 48 pp.

[109] VandaVeer, F. E., and Parr, S. W., *Ind. Eng. Chem.* **17,** 1125–6 (1925) ; *Fuel,* **5,** 309–14 (1926).

[110] Frey, A. C., *Proc. Am. Gas Assoc.,* **1925,** 1223–32.

[111] Knowlton, L. E., *ibid.,* **1929,** 1226–9.

The theoretical aspects of oxygen gasification were studied by Cerasoli [85] from the viewpoint of waste oxygen utilization. Cerasoli calculated the equilibrium composition of gases formed from $H_2O + O_2 + C$ at different temperatures. Interesting as the results may be, they are obviously only idealized cases, since equilibrium in the gas phase itself hardly takes place at the operating temperatures used, let alone equilibrium between solid and gas.

Especially in Germany, a number of processes of gas manufacture have come to a successful development in which an oxygen blast is employed. This work was made feasible by improved and cheaper processes in the production of oxygen, by the use of regenerators for cold recovery as in the Linde-Fraenkl process, and also by the availability of byproduct oxygen-air mixtures resulting from nitrogen manufacture. The processes produced gas partly for the use as city gas and partly for chemical synthesis. This type of process is essentially continuous water-gas manufacture. Experimental work on such producers has been described by Drawe,[112] and its developments have been reviewed by Millett.[113] In preliminary work, a 10 square feet generator burned lignite briquets for fuel with a deep fuel bed; steam to oxygen ratios were 2.0 to 3.4. A gas of 325 Btu content was made containing 13.2 percent carbon dioxide, requiring 55 cubic feet of oxygen per therm at a gasification rate of 31 pounds per square foot per hour. In a later paper were given results of the final plant (Lurgi type) operated on lignite under a pressure of 20 atmospheres, at a rate of 155 pounds of fuel per square

foot per hour with steam superheated to 500° C. The generator, of 12.9 square feet area, had a capacity of 340,000 cubic feet of 494-Btu gas per day. The requirements in this generator per 1,000 cubic feet of 440-Btu gas were 150 cubic feet of oxygen and 58 pounds of steam. Dried pieces of lignite containing 67.5 percent combustible matter equivalent to a coke content of 44.9 percent served as fuel.

There is a vast difference between the original and the final figures, and very interesting developments were made to bring this about. The operating pressure of the producer was raised from atmospheric to 20 atmospheres. This pressure favored the formation of carbon dioxide in the fuel bed but at the same time it promoted the formation of methane and thus raised the heating value of the gas. Furthermore, the high pressures caused higher fuel-bed temperatures, and less oxygen was required; per therm of gas the amount of oxygen necessary at 1 atmosphere was 47.7 cubic feet, and at 20 atmospheres 19.8 cubic feet. The crude gas made was readily purified at the high pressure by water scrubbing. A typical analysis before and after scrubbing is:

	BEFORE	AFTER
$CO_2 + H_2S$	30.6	3.0
Illuminants	0.6	0.5
O_2	0.1	0.1
CO	16.5	22.8
H_2	34.0	48.7
CH_4	16.3	22.6
N_2	1.9	2.3
Gross heating value, Btu per cubic foot		484

The gas left the producer at 250 to 300° C for the usual fuel with 20 to 25 percent moisture, and up to 500° for dry fuels (5 percent water). It was assumed that in the lower part of the fuel bed hydrogen, carbon monoxide, and carbon dioxide were

112 Drawe, R., *Gas- u. Wasserfach*, **69**, 1013–5 (1926); **76**, 541–5 (1933); **80**, 806–10 (1937); *Gas J.*, **203**, 95 (1933); *Arch. Wärmewirt.*, **19**, 201–3 (1938).

113 Millett, H. C., *J. Inst. Fuel*, **10**, 15–21 (1936).

formed and the highest temperature prevailed. Higher up in the bed at 700 to 800° C the reaction

$$CO + 3H_2 = CH_4 + H_2O + 49,270 \text{ calories}$$

took place.

Additional data on the Lurgi process have been given by Hubmann and by Danulat.[114] The effect of pressure on gas composition and heating values is shown

ash partly sinks in the fuel bed, partly follows the gas stream as fly ash. It is claimed that a gas containing 43 percent carbon monoxide, 45 percent hydrogen, 2.5 percent carbon dioxide, free of methane, is formed. The blast for these generators is air-steam or air-oxygen-steam. It was stated by Bosch[115] that, with air and a little steam, a power gas is produced; with oxygen-nitrogen mixtures containing 50
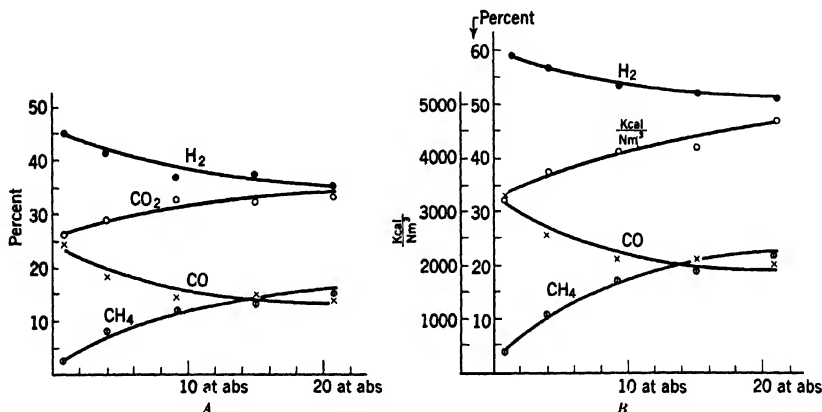
FIG. 19. Composition of the crude gas (A) and of the pure gas (B) as a function of the gasification pressure. After Danulat.[114]

in the curves of Fig. 19. The practice is to mix the oxygen with steam, superheated to 500° C, and introduce it into the producer, where the pressure is normally carried at 20 kilograms per square centimeter.

A somewhat different apparatus for total gasification with steam and oxygen is the Winkler generator of the German I.G. Using dry fuel (lignite) in finely divided form and a fairly high blast rate, the fuel bed, 1.2 to 2 meters high, is kept in a quasi-liquid condition at a uniform temperature of about 1,100 to 1,200° C. The

percent by volume of oxygen and steam, a gas suitable for ammonia synthesis is formed; with pure oxygen and ample steam high-hydrogen gases are made. No hydrocarbons are formed in any case. With shaft areas of 20 square meters the gas capacity for this type of producer is as high as 75,000 cubic meters per hour. Several modifications of the process have been described by Dolch.[83] The capacity of Winkler producers is as high as 750 tons of lignite per 24 hours for a producer 12 square meters in area. The Winkler producer compared to the Lurgi producer is

114 Hubmann, O., *Metallges. Periodic Rev*, 8, 9–15 (1934). Danulat, F., *Mitt. Metallges.*, No. 13, 14–22, 1938.

115 Bosch, C., *Chem. Fabrik*, 7, 1–10 (1934).

a high-temperature producer. Grimm [116] has reviewed the principles of Winkler producer operation and mentioned its possible applications to bituminous coals.

In a discussion of steam-oxygen operation Gwosdz [66, 117] pointed out the larger amounts of steam required by Drawe to keep the ashes from clinkering. Owing to this factor the carbon dioxide and undecomposed steam contents of the gas are high, resulting in low efficiencies. Similar discussions have been given by Von Galoczy [118] in an elaborate review of the work of VandaVeer and Parr,[109] Cerasoli,[85] and Drawe.[112] It was shown that the results of the former investigators are unreliable because of excessive heat loss through the walls of the producer with resultant progressive cooling of the fuel bed below proper operating temperatures. Von Galoczy assumed that according to Cerasoli's calculations the basic equation for steam-oxygen operation at best efficiency should be

$$3C + O_2 + H_2O = 3CO + H_2$$
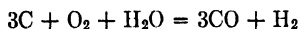
indicating a 1 : 1 ratio of oxygen to steam volumes. This ratio will naturally result in slagging of the ashes, at a fuel-bed temperature (calculated) of 1,450° C. For solid-ash-removal operations the ratio of oxygen to steam is generally 1 : 2 or higher. The logical solution for oxygen-steam operation with slagging ash was worked out in an experimental apparatus at Terni, Italy. Evidently mechanical difficulties were experienced with this installation. An alternative method of operation, removal of the ash as dust in the gas, has been described in a patent.[119]

In a later paper Von Galoczy [120] discussed at length the application of oxygen-blown producer gas to city use with its economies. An application of his system of gas production in the Thyssen-Galoczy producer has been briefly described by Paschke.[121]

Von Galoczy pointed out that the reaction of oxygen with carbon takes place at temperatures insufficient for proper steam decomposition. Hence the results obtained with an oxygen-steam blast are unsatisfactory, especially if the fuel-bed temperature is kept relatively low in order to keep the ash from fusing. In the proposed producer, the oxygen-steam mixture was preheated to a temperature adequate for steam decomposition and above the ash-fusion point by burning in it part of the fuel gas made. This process took place in precombustion chambers situated outside the producer proper. The hot combustion gases then entered the gasification shaft for simultaneous reduction of carbon dioxide and water, with slagging operations. This process was called high-temperature oxygen operation (1,800°) as compared with the low-temperature operations described by Drawe,[112] Strada, and others.[122] It was claimed that in the lower part of this producer a mixture of $2CO + 1H_2$ with little carbon dioxide or nitrogen was made. The final "oxygas" contained the gases of carbonization. It was found useful to add additional oxygen in secondary tuyères at a higher level if a high carbon monoxide gas was to be made. For the purpose of making synthesis gas, excess carbon monoxide was converted in the shaft to hydrogen by adding steam instead of oxygen

[116] Grimm, H. G., *Proc. 3rd Intern. Conf. Bituminous Coal*, **1**, 874–81 (1931).

[117] Gwosdz, J., *ibid.*, **1**, 809–39 (1931).

[118] Von Galoczy, Z., *Trans. 2nd World Power Conf.*, Berlin, **2**, 176–200 (1930).

[119] Societa italiana ricerche industriali, Brit. Pat. 306,959 (1930).

[120] Von Galoczy, Z., *Trans. World Power Conf.*, Stockholm, **1**, 111–43, 182–4 (1933).

[121] Paschke, M., *Stahl u. Eisen*, **60**, 934–5 (1940).

[122] Natta, G., and Strada, M., *Giorn. chim. ind. e applicata*, **14**, 76–86 (1932).

through the secondary tuyères and using iron-ore catalyst in the fuel. Two pilot plants of this process, one for 2 tons of coal or coke daily, one for 10 tons of coal or lignite, were reported to be in operation.

An elaborate report on gasification using steam and oxygen has been published by the British Institution of Gas Engineers.[123] The purpose of their work was primarily to investigate the possibility of adaptation of the German method, especially the Lurgi process, to British coals, using atmospheric as well as high-pressure operation. One typical point in oxygen gasification was demonstrated by Dent and coworkers:

It is seen that by supplying steam and oxygen in the ratio of 1.5 : 1 by volume the gas produced was comparatively low in carbon dioxide, while the temperatures of the fuel bed were not high enough to cause excessive clinker trouble. This was only the case, however, with a reactive coke. When using coke of low reactivity, typical of those produced from fusible coals, a temperature of 1,414° C was reached with a steam-oxygen ratio of 3.0 and the gas then contained 17.8 percent carbon dioxide. It is probable that the low temperatures obtained with reactive fuels will also prove important for the synthesis of methane under pressure. [Table II.]

[123] Dent, F. J., Blackburn, W. H., Williams, N. W., and Millett, H. C., *Inst. Gas Engrs., Commun.* **141** (1936), 76 pp.

Considerable improvement in oxygen consumption was obtained by preheating the mixture of oxygen and steam to 700° C. The oxygen consumption was estimated to be 39.6 cubic feet per therm for 700° C preheat, 46.0 cubic feet per therm for 600° C, 52.4 cubic feet for 500° C, and 58.6 cubic feet for 400° C. The estimated gas composition for a steam-to-oxygen ratio of 10 with preheat to 700° was 23.9 percent carbon dioxide, 19.8 percent carbon monoxide, 51.9 percent hydrogen, 3.0 percent methane, 0.4 percent illuminants, and 1.1 percent nitrogen, the calorific value of the gas on a carbon dioxide-free basis being 350 Btu per cubic foot. The maximum fuel-bed temperature would be 1,188° C, resulting in the decomposition of 42 percent of the total steam, yielding 267.1 therms of gas per ton of coal at a cold efficiency of 77.7 percent. Reactivation of the coke by the addition of sodium carbonate (2 percent sodium oxide) led again to better oxygen consumption values: 35.5 cubic feet per therm, at 80.9 percent cold efficiency with a fuel-bed temperature of 1,070° C.

It was pointed out that the gases obtained with heating values (carbon dioxide-free basis) even as high as 350 Btu might still be improved in heating value by pressure operation. However, the ca-

TABLE II

Influence of Steam : Oxygen Ratio on Gasification of Coke [123]

Volume of steam per volume of oxygen	1.0	1.5	2.0	3.0	5.0	7.0
Percentage composition of gas						
CO₂	0.8	4.4	7.7	15.7	23.0	37.0
CO	72.7	64.0	57.6	45.0	27.2	18.2
H₂	25.5	30.8	33.9	38.7	44.2	44.3
N₂	1.0	0.8	0.8	0.6	0.6	0.5
Steam decomposed, percent	94.5	87.6	78.5	63.2	42.3	24.7
Maximum temperature in coke, °C	1,565	1,301	1,269	1,268	1,217	1,120
Potential heat of gas as percent of total heat supplied	88.8	90.6	90.4	85.8	73.9	57.4
Oxygen used, cubic feet per therm in gas	81.2	72.9	70.2	73.5	89.0	124.0

pacity of the producer unit might be cut down by the slow rate of methane synthesis. Additional work by Dent and co-workers comprised variations in the rate of gasification, in the size of the fuel, oxygen concentration in the blast, and carbon dioxide addition to the blast. One objection to this investigation might be the small size of the apparatus used, a 3- or 6-inch tube, with an 8-inch bed of fuel. However, valuable data were given and discussed in detail.

Dolch [124] has made experiments on oxygen-steam gasification and discussed the several processes now in operation. Using a ½-square-meter fuel bed, 2 meters depth of coke, charcoal, or lignite, with oxygen-to-steam ratios of 1 : 3 to 1 : 10, and firing rates of 50 to 100 kilograms fuel per hour, no difficulties were experienced with clinkering on the grate. With coke of low volatile content, the results were:

	TEST I	TEST II	TEST III
Oxygen-steam ratio	1 2.97	1 : 4 85	1 : 9.78
Steam decomposition, percent	46.7	49.3	27.2
Cubic meters oxygen per kilogram carbon	0.63	0 635	0 77
CO_2, percent	8 0	18.5	16 8
CO, percent	40.7	19 2	6.6
H_2, percent	24.0	30.8	20.8
H_2O, percent	27.3	31.5	55.8
Cubic meters gas made per kilogram carbon	2.79	3.39	3.53
Water-gas-reaction constant, K	5.77	1.06	1.05

It is significant that for Test I water-gas equilibrium was not attained whereas for Tests II and III it was. The additional steam used served to convert carbon monoxide. With more reactive lignite or charcoal, the water-gas equilibrium was attained at the lower ratio. The thermal yield of this process is excellent.

Further references on Lurgi and Winkler

124 Dolch, P., *Wassergas*, J. A. Barth, Leipzig, 1936, 268 pp.; *Brennstoff-Chem.*, **20**, 101–11 (1939); *Feuerungstech.*, **27**, 103–8 (1939).

producers as well as on modern apparatus for manufacture of high-Btu producer gases by means of preheated blast and low-grade fuels (Pintsch-Hillebrand, Koppers, and Bubiag-Didier generators) often used for chemical synthesis work are given in Chapter 39.

Summarizing the steam-oxygen results so far obtained it appears that the actual amount of knowledge concerning the theoretical aspects is rather limited. There is need for further work, especially on the use of coal and coke in oxygen-blown producers at atmospheric or elevated pressures. Present meagre data indicate fair success for the economical production of gases for diversified chemical processes and of various heating values. The combination of low steam rates with slagging operations appears especially promising but to date has been inadequately studied.

ASH REMOVAL AND SLAGGING PRODUCERS

The importance of the ash factor in the operation of the producer process is evident from the number of times its effects have entered previous discussion.

The usual producer fuels, coal or coke, have from 3 to 15 percent ash which ha to be removed from the producer to allow continuity of operation. The ash, a residue from the combustion, is set free principally in the lower part of the reduction zone and in the oxidation zone, where the bulk of the carbon of the fuel is consumed. The temperature of the fuel bed in these zones depends on the manner of operation of the particular producer. For maximum efficiencies in the producer operation, it is desirable to have as high a temperature in the reducing zone as is possible.

Usually the mode of ash removal determines how high a temperature is allowable as a compromise between high effi-

ciency and ease of operation. If, as is usual, the ashes are to be removed in a solid form, it is essential to prevent excessive fusion of the ash which would lead to the formation of large conglomerations of fused or semi-fused ash, so-called clinkers. Such clinkers are highly objectionable for two reasons; they block the upward flow of gases in the producer bed and create irregular conditions within the fuel bed resulting in unburnt fuel reaching the ash bed and unconsumed oxygen or carbon dioxide reaching the top of the fuel bed (blow holes). Consequently poking of the producer is required. Secondly, large clinker blocks the ash flow out of the producer and thus causes irregular build-up of ashes. In producers with solid-ash-removal systems it is therefore essential to hold the fuel-bed temperatures down by the addition to the blast of "endothermic agents," such as water vapor. The fusion point of the ash determines how much cooling of the fuel bed is required. Normal operation with fuels having ash-fusion points from 1,800 to 2,800° F requires steam additions of 0.4 to 0.7 pound per pound of fuel, corresponding to blast saturation temperatures of 50 to 65° C. Correct use of steam in the blast will allow some softening of the ash so as to produce pebbly, pea-size ash nodules, which are easy to remove continuously.

The ash from the average coal consists principally of silica, lime, ferric oxide, and alumina with smaller amounts of titania, magnesia, sodium and potassium oxides, and phosphorus pentoxide. A great deal of work has been done on the fusion point of coal ashes under oxidizing and reducing conditions, both of which occur within the producer fuel bed. In general, it may be stated that high contents of silica and alumina in the ash give a high fusion point, while high contents of lime and ferric

oxide result in a low fusion point. Typical analyses of high- and low-fusion-point ashes are as follows:

	SiO_2	Al_2O_3	Fe_2O_3	CaO	Fusion Point
	%	%	%	%	°F
High-fusion	49.0	42.0	5.0	1.8	3,000
Low-fusion	28.0	8.3	49.7	5.3	2,000

Analyses and fusion points of some 2,000 American coals have been reported by Fieldner and Selvig.[125] The melting point of mixtures of the constituents silica, alumina, ferric oxide, and lime can usually be estimated from the well-known phase diagrams of these constituents [126] (Fig. 20). Hankiss [127] has given a discussion of the effect of different constituents upon ash-fusion point and producer operation. Valuable data are contained in studies of blast-furnace slags such as the work by McCaffrey.[128] (See also Chapter 15.)

It is not surprising that the alternative method of removing ashes in molten condition has seemed attractive from a theoretical point of view. The fact that the same practice is followed in blast furnaces and cupolas shows the feasibility of the idea. Producers with liquid-ash discharge are called *slagging producers*. The fuel bed of such a producer is maintained at a high temperature, thus allowing good reduction. The ash melts in the lower part of the reduction zone and in the oxidation zone, and runs down to the bottom hearth of the producer, which is periodically tapped. Following blast-furnace practice, the blast for a slagging producer is usually admitted through a number of cooled

125 Fieldner, A. C., and Selvig, W. A., *U. S. Bur. Mines, Bull.* **209** (1922), 119 pp.
126 Rankin, G. A., and Wright, F. E., *Am. J. Sci.*, **39**, 1–79 (1915).
127 Hankiss, S., *Szenkiserleti Kozlemenyek*, **1**, 41–9 (1925–6) ; *Chem. Zentr.*, **100**, 816 (1929).
128 McCaffrey, R. S., *Yearbook Am. Iron Steel Inst.*, **1938**, 189–200 ; *Am. Inst. Mining Met. Engrs., Tech. Pub.* **388**, 27–54 (1931).
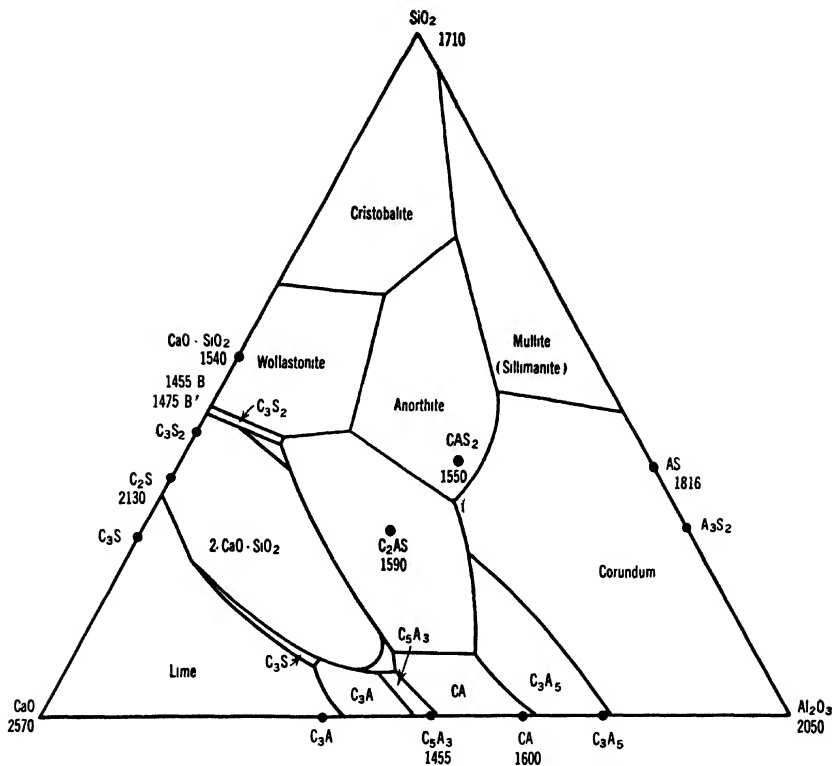
FIG. 20. Phase diagram for the ternary system CaO-Al₂O₃-SiO₂. Numerals signify melting points in degrees Centigrade.[136]

tuyères inserted around the base of the producer just above the hearth. The rate of gasification in this type of producer is high. The gas made is usually of rather low heating value owing to the use of little steam in the blast. However, in some producers of this type steam is added above the tuyère level.

Several larger slagging producers have been built abroad, some comparable in size to blast furnaces. Relatively little has been published on the mechanism of reaction in this type of producer outside of general descriptional material found in textbooks such as that of Rambush.[66] The slag obtained from these producers is often of commercial value in the manufacture of cement, building blocks, etc. Frequently the ferric oxide content of the fuel ash is such that a separate phase of molten iron underlies the molten slag and is removed through a separate tapping hole as a byproduct. It is necessary to add fluxes like limestone to the fuel of most slagging producers in order to obtain a readily flowing liquid slag, and often part of the slag, and

the iron, are mixed back with the fuel for the same purpose. Part of the reason for the relative lack of popularity of the slagging-type producer is undoubtedly the high temperature required in the process, necessitating special furnace linings and increased maintenance. As a rule slagging producers use preheated blast for the purpose of recovery of at least part of the sensible heat of the gases made, which is naturally high for operation without steam. This heat recovery necessitates recuperators. The high gasification rates of slagging producers cause entrainment of considerable fly ash in the gas especially if small fuel is used. In general the height of the fuel bed in slagging producers ranges up to 15 feet.

Experimental work on slagging producers has been reported by Smith.[129] Descriptions of German producers have been given by Markgraf [130] (Wurth type producer), Brautigam [131] (Georgs Marienhütte type producer), and Hermanns.[132] Typical conditions for these producers are indicated in Table III. A French slagging producer has been described by Servais.[133]

In special instances slagging producers are used to good advantage. One such application is gasification of low-grade shale. The Philipon producer,[134] several installations of which have been made in France, is a typical example, and good detailed descriptions have been given (Table

129 Smith, C. D., *U. S. Bur. Mines, Tech. Paper* **20** (1912), 14 pp.

130 Markgraf, H., *Stahl u. Eisen* **38**, 703 7 (1918).

131 Brautigam, M., *ibid.*, **38**, 186-9 (1918).

132 Hermanns, H., *Z. Ver. deut. Ing.*, **64**, 351-4 (1920).

133 Servais, E., *Rev. mét.*, **19**, 596-9 (1922).

134 Dessemond, A., and Mayencon, M., *Chaleur et ind.*, **9**, No. 102, 272-7 (1928). Philipon, H., *Rev. ind. minérale*, **317**, 125-37 (1934). Estival, J., *Génie civil*, **49**, 405-7 (1936). Van Oirbeek, J., *Rev. mét.*, **33**, 303-8 (1936).

TABLE III

TYPICAL OPERATING CONDITIONS FOR SLAGGING PRODUCERS [130, 131]

	Wurth	G. Marien- hütte
Coke gasified, metric tons per day	50	30
Slag added, percent by weight	11	17
Air used, 1,000 cubic feet per metric ton	115	134
Steam used, percent by weight of air blast	32	0
Gas made, 1,000 cubic feet per metric ton	156	164
Dust, percent by weight	9.6	2.4
Slag, percent by weight	13.3	18.0
Iron, percent by weight	0.3	3.2
Temperature blast, °C	240	55
Temperature hot gas, °C	700	800
Pressure loss, centimeters H_2O	55	33
Percentage gas composition		
CO_2	2.0	0.6
CO	32.0	33.4
CH_4	0.5	0.5
H_2	7.5	0.9
Net Btu per cubic foot	136	121.6
Cold efficiency, percent	79.0	72.7
Sensible heat of gas, percent	16.0	18.6
Percentage composition of slag tapped		
SiO_2	37.0	32.3
Al_2O_3	24.3	....
Fe	1.6	1.6
Mn	1.3	4.9
Ca	21.1	21.7
Mg	2.2	...
S	0.95	0.62
Percentage composition of iron tapped		
Si	3.0	....
Mn	2.91	9.27
P	1.42	9.25
S	0.07	0.022

IV). To preheat the blast up to 400° C the sensible heat of the gas made was utilized. To supply preheat from 400 to 800° C, about 15 percent of the gas make was burned in a silica recuperator. The efficiency obtained is remarkably good considering the low-grade fuel and the enormous throughput. The operation was

TABLE IV

CONDENSED DATA FOR A PHILIPON PRODUCER. 1.50-meter internal diameter at the tuyère level.[134]

Percentage composition of charge (10–50 mm size)	41.5 shale of 50 to 60 percent ash
	25.0 low-grade coke of 28 to 30 percent ash
	22.8 limestone
	7.1 iron
	3.6 slag
Percentage composition of gas	4.5 CO_2
	31.0 CO
	4.0 H_2
	2.0 CH_4
	58.5 N_2
	1,260 kilogram calories gross heating value per cubic meter (132 Btu per cubic foot)
	1,210 kilogram calories net heating value per cubic meter (126 Btu per cubic foot)
Percentage composition of slag (used for cement)	35.0 SiO_2
	22.5 Al_2O_3
	40.0 CaO
	1.0 MgO
	1.5 FeO
Percentage composition of iron	3.0 C
	0.4 Mn
	10.0 Si
	0.5 P
	0.03 S
Charge, metric tons per day	100 to 150
Gas make per day, 1,000 cubic meters	200 to 300
Gas make per 1,000-kilogram charge, cubic meters	1,810
Slag per 1,000-kilogram charge, kilograms	417
Iron per 1,000-kilogram charge, kilograms	147
Air per 1,000-kilogram charge, cubic meters	1,340
Gasification rate, kilogram per square meter per hour	3,550
pounds per square foot per hour	728
Temperature blast, °C	400 (to 800)
Temperature top gas, °C	200 to 400
Temperature fuel bed at tuyères, °C	1,800 to 2,000
Cold efficiency, percent	71.6

claimed to be uniform as long as the blast temperature was constant. Blast-temperature variations readily caused freezing of the slag near the tuyères, due to the shifting of the isothermal zones. The use of this type of a producer for the recovery of metals from smelting residues has been discussed by Philipon,[134] van Oirbeek,[134] and Rambush.[135]

Tests on slagging producers have been described by Heczko.[136] Using coke with additions of some 30 percent of mixed slags a gas containing 0.5 percent carbon dioxide, 33.3 percent carbon monoxide, 2.3 percent hydrogen, and 64.6 percent nitrogen was made, having a calorific value of 1,050 to 1,090 calories per cubic meter (110 to 114 Btu per cubic foot); the production was 4.2 cubic meters of gas per kilogram of coke with a cold efficiency of 69.9 percent. In these tests the temperature of the outlet gases was 800° C.

In a discussion of different types of producers Guillon[66, 137] pointed out that in successful slagging-type producers the blast inlet area is one-hundredth or less of the cross-sectional area of the producer shell, resulting in air velocities as high as 100 meters per second based upon cold air. It was claimed that with high blast velocities the carbon monoxide content increased in cupolas, and the same was assumed to hold for producers. Temperatures up to 2,000° C were obtained by preheating the blast to 800 to 1,000° C. The principle of high blast velocity is of great interest and will be discussed later.

135 Rambush, N. E., and Rhon, F. F., *Trans. Inst. Chem. Engrs.*, *London*, **9**, 3–15 (1931); *Can. Chem. Met.*, **15**, 319–21 (1931).

136 Heczko, A., *12th Congr. chem. ind.*, *Prague*, **1932**, 25–9; *Chimie & industrie*, Spec. No., June 1933, pp. 420–6.

137 Guillon, H., *Chaleur et ind.*, **16**, 183–4, 518–24, 560–2 (1935), **17**, 153–6, 191–7, 230–4, 281–5, 451–4 (1936), **19**, 344–8, 533–40 (1938).

An interesting application of slagging operation with high blast velocity is the Gohin-Poulenc type vehicular producer. The molten ash is collected in the base of the shell where it solidifies to a ball and is removed periodically.

It has been mentioned before that efforts have been made to apply oxygen blast to slagging producers, but information on this subject is scanty.

Summarizing, it appears that the use of slagging operations on a large scale offers a wide field of application as yet barely touched. Extremely high throughput rates hence low overhead, recovery of valuable byproducts, the possibility of utilizing lowest-grade fuel, and good efficiency are among the principal advantages.

HIGH-SPEED OPERATION

In the foregoing section the effect of high-speed air injection into the producer was briefly mentioned. Work in Russia and France has given indication that hitherto unknown rates of operation can be obtained in specially constructed producers by high-speed injection of air or air-oxygen blast. This work is based on no very well-established theory, and no investigations along these lines have been conducted in the United States.

Two Russian investigators, Grodzovskii and Chukhanoff,[18] pointed out the customary limitation of the producer reactions by the slow rate of reduction of carbon dioxide (or water) to carbon monoxide (or hydrogen) and showed that these factors limit the rate of gasification even at high combustion-zone temperatures ($1,700°$ C) to about 80 pounds of coke per square foot per hour. This slow rate of reduction was attributed to surface films. According to Grodzovskii and Chukhanoff, high gas velocity will cause the mechanism of the reaction to change to direct production of

carbon monoxide without intermediary dioxide formation. The only limiting factor in monoxide production then is the rate at which oxygen can reach the carbon surface. Thus high-velocity blast will create ideal conditions for monoxide production, and actual experimental curves show an increased monoxide : dioxide ratio for
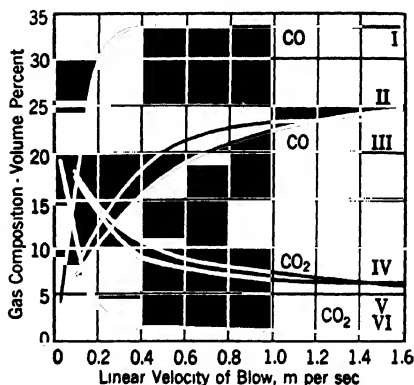
Fig. 21. Relationship between gas composition and linear velocity of the blow for various carbonaceous materials.[18]

I, activated charcoal. IV, electrode carbon
II, coke. V, coke.
III, electrode carbon VI, activated charcoal

increased blast rates. Addition of oxygen to the blast air improves this ratio even more (Figs. 21 and 22).

Furthermore, it was shown that in the combustion zone the reduction of steam by carbon was greatly accelerated at high rates (Fig. 23) and ideal conditions were obtained for rapid production of producer gas of high-Btu value. For a limited fuel-bed height, in an up-draft type producer, there might be a minimum in carbon monoxide content of gas when changing over from the normal low blast rate to the high blast rate. It was essential for effective high-blast operation to have a dense fuel bed, preferably with small fuel. Ash
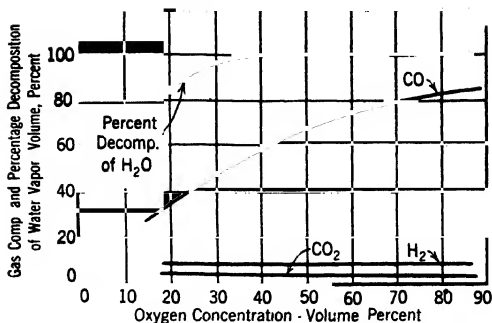
Fig. 22. Relationship between gas composition and oxygen concentration in the blow.[16] Activated charcoal, 1–3 millimeters. Stove area, 3.2 square centimeters. Water vapor in inlet gas, 13 percent. Inlet blow velocity, 0.9 meter per second.

was carried along with the gas to a large extent. Small-scale tests with coal, coke, and other fuels (150 to 200 millimeters deep fuel bed, 0.038 square meter or 0.12 square meter area) showed that blow velocities as high as 3.2 meters per second

Fig. 23. Relationship between gas composition and linear velocity of steam-air blow.[18] Activated charcoal, 1–3 millimeters. Stove area, 3 2 square centimeters. Water vapor in inlet gas, 14 percent.

(cold blast, calculated on free area of shell) could be used corresponding to combustion rates as high as 3.0 tons per square meter per hour (600 pounds per square foot per hour) for coke and 7.0 tons per square meter per hour for a 1 : 1 coal-coke mixture. Under these conditions the composition of the final gas (without steam additions to the blast) was 4 to 9 percent carbon dioxide and 24 to 31 percent carbon monoxide, heating value 1,000 to 1,300 calories per cubic meter (104 to 136 Btu per cubic foot).

A second development on the basis of the high-velocity theory was the so-called pitless producer. Experiments showed that, by blowing oxygen with or without nitrogen or steam in a cavity of an anthracite block, carbon monoxide would be made at a rate increasing with higher gas velocity: for linear jet velocities of 35 and 180 meters per second the monoxide content rose from 50 to 90 percent, and the dioxide content decreased from 50 to 10 percent. In a semi large-scale test, two water-cooled tuyères were set opposite each other. One supplied the blast, and the other fed the fuel, which consisted of a mixture of coal dust, refuse, peat, and tar, extruded as cylinders, 60 millimeters in diameter and 300 millimeters long. The nozzle velocity of the blast (64 percent oxygen) was 500 meters per second. The resulting gas had 16 percent carbon dioxide, 0.6 percent oxygen, 33 percent carbon

monoxide, 21 percent hydrogen, 0.7 percent methane, 27 percent nitrogen, 1,600 calories (167 Btu) heating value, for a combustion rate of 1,200 tons carbon per square meter nozzle area per hour. For 90 percent oxygen blast the gas analysis was 13.6 percent carbon dioxide, 0.3 percent oxygen, 51 percent carbon monoxide, 28 percent hydrogen, 0.2 percent methane, 7 percent nitrogen, 2,350 calories per cubic meter (246 Btu per cubic foot), with a combustion rate of 1,790 tons carbon per hour per square meter.

The results of the work of the Russian investigators are very novel indeed. It has been verified by Karzhavina [19] as far as the theoretical aspect is concerned. Rates of operation obtained in the Philipon and the Gohin producers seem to indicate that the deductions as to possible operating rates published by Grodzovskii and Chukhanoff are more than mere speculations.

Among the newer types of small producers for making gaseous fuel for automobile engines, the Gohin-Poulenc type and various modifications are of particular interest. The fuel is contained in a vertical shell; the blast is introduced through a horizontal tuyère inserted in the lower part of the producer almost to the center of the shell. The gas outlet is approximately at the same elevation and opposite the tuyère. Because of the high blast entrance velocity a concentrated fire is created at a high temperature, 1,500 to 2,000° C, in which the conversion of the fuel to carbon monoxide takes place. The unburnt fuel surrounding the hot spots protects the unlined walls. The gas velocity is of the order of 100 and more méters per second. The grate (tuyère) area is 3 square centimeters; the distance between tuyère tip and gas outlet, 15 centimeters. Some variations of the Gohin-type pro-

ducer use preheated blast. The thinness of the fuel bed and the evident efficiency of this type of apparatus seem to indicate that the classical producer theory does not apply,[97] and that this class of producer is of the high-speed type with direct carbon monoxide production. It is typical that with slower blast the carbon dioxide increased to 12 percent from a normal 2 percent. The ashes in Gohin producers fuse and run down into the base of the producer.

Thring [98] has conducted a very interesting investigation of the cross-draft (or oblique-draft) producer on full scale as well as on a model (micro producer). It is his contention that the remarkable performance of this type of producer is due not so much to high entrance gas velocity as to the position of the air nozzle in the center of the fuel bed with consequent avoidance of all wall losses and higher reaction temperature. On a cross-draft producer 20 by 14 by 60 inches, rectangular in shape, 3-hour tests were conducted with ⅜ by ³⁄₁₆ inch coke as fuel. The blast rate was kept at 40 cubic feet air per minute; moisture to the extent of 40 percent of the weight of the carbon was added. While the blast velocity (nozzle size) was varied from 30 to 200 feet per second the calorific value of the gas varied only from 115 to 124 Btu per cubic foot, the temperature near the inlet from 1,640 to 1,620° C, the gas outlet temperature from 420 to 550° C, and the back-pressure from 4.5 to 23 inch water gage. The last word on the mechanism of this process has not yet been spoken.

As a final remark on this process of high-speed gasification it may be of interest to point out that the speed of the air entering blast-furnace tuyères is of the same order of magnitude as in the high blast velocity producers, namely, several

hundred feet per second. Both from the point of view of blast-furnace operation and of further development of high-speed gasification a coordination of data seems most desirable. The typical effect of an increase of carbon dioxide near the tuyère with a lowering of the wind shows up clearly in the curves of Perrott and Kinney presented in a book on blast-furnace operation by Sweetser.[138]

USE OF CARBON DIOXIDE IN BLAST

In earlier years it was frequently suggested that carbon dioxide be substituted for water vapor in the operation of the producer. No doubt the addition of carbon dioxide in the form of flue gases, lean blast-furnace gas, etc., will produce the same effect as steam addition and cool the fuel bed to the desired degree. It is obvious, of course, that, unless pure carbon dioxide is used, it will carry with it a large amount of inert nitrogen, resulting in high blast velocities, requiring higher fuel beds for proper heat exchange, and making a larger volume of low-Btu producer gas of high gravity. Essich[139] calculated that the temperature of the gas from an air-blown producer (no steam) can be reduced from 1,000 to 500° C by adding 1 volume of carbon dioxide to 5 volumes of oxygen or by using a blast composition of 3.5 percent carbon dioxide, 17.5 percent oxygen, and 79 percent nitrogen. Furthermore, the heat of the flue gases can be partly recovered and the carbon dioxide content of the blast can be increased 0.5 percent for each 100° flue-gas heat. The fuel saving that would be realized in this manner is the ratio 100 (CO_2) : $(CO_2 + O_2)$. No experiments were conducted.

Similar discussions and calculations are found in the literature.[140]

Experiments on the use of blast-furnace gas as the endothermic agent have been described by McDermott.[141] The results were not encouraging since clinkering difficulties appeared and smooth operation was obtained only by alternate blowing with air and gas. Some additional work on this subject by Swardt has been reported by Walker.[80] It seemed to indicate an improvement in the cold efficiency from 68 to 84 percent (maximum) when adding from 20 to 25 percent cold exhaust gases to the blast of a 9-horsepower "National" producer and engine operating on charcoal. A gas composition of 1.7 percent carbon dioxide, 4.3 percent oxygen, 20.3 percent carbon monoxide, and 73.7 percent nitrogen was obtained with zero exhaust gas in the blast, and the respective percentages with 20 percent exhaust gas in the blast were 2.2, 3.7, 21.5, and 72.6. As the exhaust-gas percentages increased, the values of gas were impaired. In view of the peculiar compositions of the gas, indicating that leakage took place, not too great a value can be placed upon these results. Indications from this method of operation do not offer great promise.

PREHEATED BLAST

In several instances the advantage of a preheated blast has been pointed out. A preheated blast benefits operation in that there are obtained a lower outlet gas temperature from the producer, a higher fuel-bed temperature resulting in better carbon dioxide reduction, and better heat effi-

[138] Sweetser, R. H., *Blast Furnace Practice,* McGraw-Hill Book Co., New York, 1938, pp. 151–3.

[139] Essich, O., *Feuerungstech.,* 8, 184–5 (1920).

[140] Gwosdz, J., *Feuerungstech.,* 9, 73–84 (1921). Hudler, J., *Gas- u. Wasserfach,* 64, 475–9 (1921). Czerny, R., *Feuerungstech.,* 15, 13–7 (1926). Wislicenus, W., *Arch. Wärmewirt.,* 9, 331–4 (1928).

[141] McDermott, G. R., *Blast Furnace Steel Plant,* 13, 344–6 (1925).

ciency made possible by recovery of sensible heat from the outlet gases. It is realized that blast preheat can be utilized to full advantage only with high fuel-bed temperatures and therefore slagging ash operation is usually required. For this, blast preheat is almost an essential in view of the danger of freezing the slag by undesired temperature variations. Furthermore, it is the only way to raise the efficiency of slagging producers operated without steam additions to the blast.

Blast preheat usually takes place in recuperators, for which a number of constructional types are available. Occasionally regenerators are used to preheat the blast following along the lines of blast-furnace practice. It is beyond the scope of the present discussion to go into the details of this choice. The Pintsch-Hillebrandt generator for high-Btu gas supplies the heat required for continuous steam decomposition in the fuel bed by preheating the blast, composed of steam plus part of the production gas, to a temperature of 1,300° in a hot blast stove.

FUEL FACTORS

The influence of the fuel on the reactions occurring in the producer has been mentioned frequently in previous discussions. The principal items of interest in this respect are the following: (1) moisture content; (2) volatile matter; (3) ash content and analysis; (4) reactivity; and (5) size and size distribution.

Moisture as well as the *volatile matter* in the fuel are removed in the upper parts of the producer fuel bed. For the removal of the bulk of the volatile matter a temperature of 400 to 600° C is adequate. With fuels containing little volatile matter, such as high-temperature coke and charcoal, the effect on the gas make is inconsiderable. In the lower layers of the reduction zone the hydrogen of the coke is driven off as hydrogen gas or methane. Moisture will tend to cool the gases, thus preventing to some extent the carbon monoxide to carbon dioxide reversal reaction. With fuels like coal, lignite, and others of high volatile content, the carbonization process taking place in the upper distillation zone of the producer causes the producer gas to be enriched by the volatile products of carbonization, gas and tar vapors. Both these products tend to increase the heating value of the final producer gas, especially when the gas make is burnt directly without previous cleaning. All constituents normally present in carbonization gases can be found in such producer gas, depending only on the temperature at which the carbonization was performed. With fairly thin fuel beds, or with abnormally hot fuel-bed tops, the gases evolved from the volatile matter of the fuel are considerably cracked, have a dark color, and contain a large amount of lampblack; with thick fuel beds, they resemble crude coke-oven gas and are greenish brown in appearance. The heating value of coal producer gas is raised from 120 to 160 Btu by the presence of the carbonization gases, and the tar vapors contribute an additional 30 Btu to the mixture.

The carbonization process will leave a carbonaceous residue which assumes the major role in the producer proper. Depending on the nature of the coal, this residue may be more or less caked to a coherent mass. For the sake of uniformity of operation such a mass should be broken up to smaller particles to prevent channeling in the fuel bed. Various poking devices serve for this purpose. A coal with excessive caking tendency should be avoided. Sizing of fuel if it undergoes a coking process is naturally of less impor-

tance, since the size of the fuel in the reduction and oxidation zones cannot be controlled under these conditions. The coke resulting from producer carbonization is usually similar to low-temperature coke. Carbonization becomes more than an incidental enrichment in processes for complete gasification with production of high-Btu or synthesis gases. Controlled carbonization of producer fuel is the aim of the Bubiag-Didier and Koppers types of generators for making synthesis gas ($2H_2 + CO$). The low-temperature carbonization gases made in the Bubiag-Didier generator are used to supply external heat to the generator shaft; in the Koppers process they are cracked to supply additional hydrogen to the synthesis gas.

Since the presence of tarry matter complicates the cleaning of producer gas, a number of producers of the down-draft or double-draft type have been designed to pass the distillation gases from the "green" fuel through the hotter parts of the fuel bed, thereby causing the tar vapors to be cracked into smaller molecules. In the down-draft producer the air enters the fuel bed on top, and the gas leaves below. In the double-draft producer the flow of the gases is upward in the lower half, downward in the upper half of the fuel bed, the gas finally leaving at the midpoint of the fuel bed.

With wet fuels like peat, wood, and sometimes coal, the moisture content may be high enough to require more than the sensible heat of the gas for vaporization. The additional heat is then supplied by a combustion of a portion of the fuel to carbon dioxide, causing the heating value of the final gas to decrease and the carbon dioxide content to increase.

Depending on the volatile-matter content of the fuel, the tar yield obtained from gasification of coals will vary and is found to be 80 percent of the usual laboratory tar yield (Rambush) determination.

The *ash content* of the fuel is an important factor for various reasons. The fusion point of the ash determines the practical amount of steam necessary in the blast to prevent the ash from clinkering. In turn this amount of steam influences the thermal efficiency of the producer. In slagging producers the fusion point of the ash and its composition are instrumental in determining the amount of flux required. Ash compositions may affect the reactivity of the fuel and its catalytic action on the water-gas reaction. High ash content of the fuel tends to raise the losses of fuel as carbon in the ashes. Heat loss in the ashes leaving the producer is generally negligible for solid-ash removal but appreciable for slagging producers. Ash acts as a diluent of the fuel bed, especially in the lower layers, and consequently influences the height of the oxidation and reduction zones.

Probably the most important single fuel factor is *reactivity*. Its preponderant effect especially on the reactions in the reducing zone has been mentioned repeatedly. The reactivity factor includes such influences as physical conditions of the carbon —size, porosity, crystalline structure—and chemical conditions—hydrogen content, ash content, and added catalyst such as sodium carbonate. Reactivity affects producer efficiency, gas composition, and producer capacity.

A good set of papers on the reactivity of different coals with results in actual producers is that of Gevers-Orban.[142] The "reducing power" of the fuel increases in the order natural coke, activated coke, alkaline coke, activated alkaline coke. Coke made of high-volatile coal at low

[142] Gevers-Orban, E., *Rev. universelle mines,* 10, 313–20, 347–52, 376–86 (1934).

temperature, 575° C, reduces more readily than coke made at 850° C. The use of different types of coke, anthracite, coal, catalyzed fuels, etc., in vehicular producers is discussed in detail in a later paper.[143]

Size and *size distribution* influence producer-gas manufacture primarily in their effect on the reactivity of the fuel and secondarily by reason of their influence on the ease of operation. Uniform sizing of fuel promotes uniform flow of gases across the entire area of the producer and uniform gas manufacture. Lack of uniformity of the fuel leads to segregation of sizes in distinct spots of the fuel bed, channeling of the blast with ensuing blow holes, local overheating and clinkering, high ash loss, and other objectionable conditions. The presence of excessive amounts of fine particles (dust) in the fuel leads to fuel losses with the gas stream. In producers operating with fine fuel, like the Winkler producer, special arrangements are made to recover the entrained material.

COMPLETE GASIFICATION AND MANUFACTURE OF SYNTHESIS GAS

Although producer gas has previously been defined as a gas with carbon monoxide as principal combustible component, made by incomplete combustion of carbonaceous fuel, a wider definition is possible which includes a number of processes on the boundary between producer-gas and water-gas manufacture. Producer gas may be defined as the product of continuous complete gasification of carbonaceous fuel. Examples of processes which might be termed typical of continuous water-gas manufacture have already been mentioned under oxygen steam-blown producers. Instead of considering the product of such

generators as producer gas minus inert nitrogen it can be taken as blue water gas $(CO + H_2)$ made by a process in which sufficient heat is continuously liberated in the fuel bed by the addition of oxygen to the steam and thus causing the exothermic reaction of $C + O_2$ to compensate for the heat required in the endothermic reaction of $C + H_2O$. Other means for supplying the heat required for the water-gas reaction are found in preheating the blast or in applying external heating to the generator shaft. Several varieties of gas are made in this manner; the high-pressure Lurgi process, for example, is one in which carbon monoxide is no longer the principal combustible constituent of the gas.

The development of this type of process abroad has advanced very rapidly because of the economic need for complete gasification of low-grade fuels such as lignite and the production of gas not only for combustion but also for chemical synthesis. The Fischer-Tropsch process for synthesis of hydrocarbons (see Chapter 39) requires enormous amounts of a gas mixture of 2 parts of hydrogen with 1 part of carbon monoxide. An entirely new gas industry, belonging without too much stretching of the imagination to the producer-gas field, has been created for the production of this synthesis gas $(CO + 2H_2)$.

A voluminous literature has grown up around this work; a few of the types of processes employed may be described briefly. In a review of water-gas and synthesis-gas manufacture from coal Schultes[144] enumerated the methods for making synthesis gas as follows:

1. By intermittent blue-gas manufacture, adding hydrogen by catalytic conversion of carbon monoxide or by decomposition of coke-oven gas.

143 Gevers-Orban, E., *ibid.*, **13**, 249–59 (1937).

144 Schultes, W., *Glückauf*, **72**, 273–85 (1936).

2. By continuous water-gas manufacture.
   (a) Directly at low temperature (650°) to give $CO + 2H_2$, using an oxygen blast.
   (b) At medium pressure with oxygen blast (high pressure results in methane formation).
   (c) In special producers with oxygen blast and increased fuel reactivity.
   (d) Directly in slagging producers.
   (e) From carbon monoxide of slagging producers with subsequent partial conversion.
3. By decomposition of coke-oven gas in special furnaces, in water-gas generators, or by the effect of oxygen.
4. Directly by low-temperature carbonization and cracking of the gas with or without external heating.

Among the better-known methods with continuous operation is the Lurgi process, which is operated at 1 atmosphere gage pressure and is claimed [114] to give a gas with 29 percent carbon dioxide and a 2 : 1 ratio of hydrogen and carbon monoxide. The Winkler process (semi-floating fuel bed) develops from gas coal a gas of 18 percent carbon dioxide, 42 percent carbon monoxide, and 37 percent hydrogen. Additional conversion of carbon monoxide is required to yield a suitable synthesis gas.

A process involving a slagging producer operated with an oxygen blast has been proposed by von Galoczy. Supplying heat to the fuel bed by preliminary combustion of a portion of the gas in the oxygen blast, a gas having 6 percent carbon dioxide, 64 percent carbon monoxide, and 22 percent hydrogen can be made. More carbon monoxide conversion is required to obtain a satisfactory gas for synthesis.

The Bubiag-Didier process uses a vertical refractory shaft in which the descending coal is subjected to external heat and thereby successively dried, carbonized at low temperature with separate low-temperature gas removal, degassed for methane and hydrogen removal, these gases

cracked by the hot coke, and blue water gas made by ascending steam. From a gas coal is produced gas containing 9 percent carbon dioxide, 28.8 percent carbon monoxide, and 57.6 percent hydrogen at a rate of some 2,000 cubic meters per ton of coal. The external heating is accomplished by producer or low-temperature carbonization gas. Coals of negligible caking tendency should be used.[145]

In the Pintsch-Hillebrand process heat is supplied for the water-gas reaction by preheating the blast, consisting of steam and recirculated gas, in a set of gas-heated hot blast stoves. The German Koppers Company has a recirculation process somewhat like the Pintsch-Hillebrand process.

The nature of the fuel, especially its hydrogen content, is a deciding factor in the economic success of synthesis-gas manufacture, and the choice of system is closely connected with the type of fuel. Dolch has dealt with this problem exhaustively [146] and has pointed out that the high reactivity of lignite permits the production of synthesis gas in one step. Dolch [124] has also ably discussed the different processes for making high-heating-value gas, which have been reviewed by Brückner [66] and by Rosendahl.[147]

PRODUCER-GAS PROPERTIES

Producer-gas composition varies with the mode of manufacture. Since producer gas is obtained generally from either coal or coke, the following discussion will be limited to the properties of these two types

[145] Thau, A., *Brennstoff-Chem.*, **16**, 61–7 (1935). Allner, W., *Gas- u. Wasserfach*, **78**, 438–56 (1935).
[146] Dolch, P., *Brennstoff-Chem.*, **20**, 101–11 (1939); *Feuerungstech.*, **27**, 1–5, 44–51 (1989).
[147] Rosendahl, F., *Oel u. Kohle ver. Petroleum*, **36**, 340–9 (1940).

of gases as formed in the up-draft-type producers.

COMPOSITIONS

Typical compositions for cleaned coke and coal producer gas are:

	CO_2	ILLUMI- NANTS	CO	H_2	CH_4	N_2	GROSS BTU	NET BTU
	%	%	%	%	%	%	(dry, 60° C, 30 in.)	
I Coke gas	5	0	28	12	0.5	54.5	134	128
II Coal gas	4	0.5	28	14	3	50.5	178	166

Besides these major components producer gas contains minor components, some of which are of importance.

Sulfur Compounds. A review of the literature on this subject by Crabtree and Powell [148] shows that the hydrogen sulfide content of coal producer gas ranges from 1.0 to 3.0 percent, depending on the type of coal, producer temperatures, air-steam ratio, and other factors. The distribution of sulfur in coal producer gas has been discussed by Kaufman.[149] It was claimed that hydrogen sulfide and carbon disulfide occur in the ratio 2 : 1, depending, however, on the coal composition. Private information reveals 105 grains of hydrogen sulfide and 18 to 22 grains of organic sulfur per 100 cubic feet in producer gas made from coal of 1.6 percent sulfur content and 36 percent volatile matter, and from 40 to 70 grains of hydrogen sulfide and from 7 to 10 grains of organic sulfur per 100 cubic feet in producer gas from coke of 0.6 to 0.7 percent sulfur content. The coal ash contained 0.3 percent sulfur, the coke ash 0.07 percent. An elaborate paper, unfortunately rather inaccessible because of the language, has been published on sulfur in producer gas by Berg,[150] who reviewed thoroughly the analytical methods for determination of sulfur and its compounds (H_2S, SO_2, SO_3, SiS_2, CS_2, COS) in producer gas. Results cited of various other authors [151] indicated that a conversion of coal sulfur to gas sulfur of 76 to 99 percent takes place with sulfur contents of coal from 2.80 to 0.8 percent. A detailed sulfur balance made on two coal producers of 2.6-meter inside diameter showed that 92.5 and 94.1 percent of the coal sulfur appeared in the gas when the sulfur content of coal was either 0.91 or 1.00 percent, respectively.

The gas sulfur was distributed as follows (5-day test):

	GRAMS PER CUBIC METER	PERCENT OF TOTAL SULFUR
Flue dust	0.14	6.0
Tar	0.02	1.0
H_2S	1.72	71.7
SO_2	0.35	14.4
Organic S	0.17	6.9
	2.40	100.0

COAL SULFUR	PERCENT OF COAL	PERCENT OF TOTAL SULFUR
Sulfate	0.01	1.0
Pyrite	0.56	56.0
Organic	0.43	43.0
	1.0	100.0

148 Crabtree, F., and Powell, A. R., *Bull. Am. Inst. Min. Met. Engrs.*, **153**, 2087–92 (1919).

149 Kaufman, C. F., *Chem. & Met. Eng.*, **22**, 544 (1920).

150 Berg, T., *Jernkentorets Ann.*, **144**, 213–72 (1930) ; *Stahl u. Eisen*, **50**, 942 (1930).

151 Jung, A., *Ver. deut. Eisenhuttenleute, Stahlwerksausschuss Ber.*, **83** (1924), 4 pp. Bronn, J., *ibid.*, **89** (1925), 3 pp.; *Stahl u. Eisen*, **46**, 78–80 (1926).

Operating data were as follows:

PERCENTAGE COMPOSITION OF THE GAS

CO_2	5.1
O_2	0.3
CO	27.1
CH_4	4.1
H_2	9.6
N_2	53.8
	100.0

Gas temperature, °C	603
Gas moisture, grams per cubic meter	40.2
Operating rate, ton per hour	0.88
Steam consumption, percent of coal weight	20 to 25

Practically all the organic sulfur in the gas was present as carbon oxysulfide.

It should be added that the original purpose of Berg's work was to find a process suitable for lowering the sulfur content of producer gas. A number of tests were described and the literature was discussed relative to this subject. An effort to accomplish the purpose by adding lime to the coal was unsuccessful. The significance of small quantities of hydrogen sulfide in producer gas lies chiefly in the corrosive property of hydrogen sulfide itself or of its products of combustion, as well as in the contamination of metallic baths with sulfur when heated with producer gas.

Nitrogen Compounds, Ammonia. At one time the ammonia content of coal producer gas was of outstanding importance. Owing to economic conditions, ammonia recovery from byproduct producers such as the Mond and Power Gas types has now become rare.

A comprehensive literature concerned with the effect of various operational factors on the ammonia content of producer gas from byproduct recovery systems is available and has been ably reviewed by Rambush. It may be assumed, for a nitrogen content of an average coal of 0.5 to 2 percent, that mere heating of the coal between 500 and 900° C liberates up to 30 percent of the nitrogen, chiefly as ammonia, and that the best ammonia yield is obtained at 800° C. The remainder of the nitrogen remains in the coke. During the gasification of the coke, especially at relatively low temperatures and in the presence of ample steam, a conversion of the nitrogen in the coke to ammonia can take place to an extent equal to 67 percent of the nitrogen in the coal. Again a temperature of 800° seems best for this ammonia formation. The ammonia at 800° is not in thermal equilibrium with nitrogen and hydrogen, hence the gas should be cooled rapidly for maximum yield. Ash constituents and the reactivity of the coke affect the nitrogen conversion. Addition of lime to the coal increases the ammonia yield. The actual recovery of ammonia, depending on the steam-air ratio, will range from 30 to 60 percent for 0.8 to 4.4 pounds of steam in the blast per pound of fuel. Mond producer gas has a peculiar composition due to the high steam ratios usually employed: 17 percent carbon dioxide, 11 percent carbon monoxide, 24 percent hydrogen, 3 percent methane, and 45 percent nitrogen.

Nitrous Oxide. In recent years the presence of small amounts of nitrous oxide in fuel gases has attracted a great deal of attention because of the gum-forming tendency of nitrous oxide in the presence of oxygen and certain unsaturated hydrocarbons. Nitrous oxide is formed to a small extent whenever nitrogen and oxygen are present in a gas at temperatures of 600° C and above. The nitrous oxide concentration in producer gas is from zero up to 70 grams per million cubic feet, depending on the condition of the fire bed. It has been claimed that in the absence of

blow holes the nitrous oxide content of producer gas is zero.

Hydrogen Cyanide. Other gaseous nitrogen compounds, such as hydrogen cyanide, can be expected in producer gas in low concentrations. Their presence has not been studied to any extent.

COMBUSTION PROPERTIES

On the basis of the well-known properties of the constituent gases the combustion qualities of producer gases can readily be calculated. For complete combustion for the above two typical compositions, there is found:

	COKE GAS	COAL GAS
	I	II
Cubic feet of air per 100 cubic feet gas	100	110
Cubic feet of combustion gas per 100 cubic feet gas including water vapor	180	189
Cubic feet of combustion gas per 100 cubic feet gas exclusive of water vapor	167	168
Percent carbon dioxide in dry combustion gas	20	21.8

The *flame temperatures* of the two gases corrected for dissociation may be calculated to be (cold gas) 3,060° F and 3,470° F, respectively.

The rate of *flame propagation* of producer gas is of the order of 0.6 to 0.8 foot per second; the rate for hydrogen is as high as 9 feet per second, and that for carbon monoxide 1.7 feet per second. The *explosive limits* are approximately between 20 and 70 percent gas in mixture with air.

Another important factor in determining the effect of flames is the *radiation power* of the nonluminous flame, which depends on the relative concentrations of carbon dioxide and water in the combustion gases. At the usual combustion temperatures of producer gas (3,000 to 3,500° F) and under customary large-scale combustion conditions with the product Pl (P is partial pressure of carbon dioxide or water in atmospheres; l is mean thickness in feet of radiating gas) at 0.25 or more, the radiating power of carbon dioxide is surpassed by that of water. Charts published by Hottel [152] indicate that, at 3,000° F with $Pl = 1.0$, the radiating power of carbon dioxide is about 23,000 and that of water 42,000 Btu per square foot per hour. At Pl values lower than about 0.25 this condition is reversed. This result from the modern treatment of nonluminous combustion is at variance with the formerly accepted theory that a carbon monoxide flame radiates better than a hydrogen flame.[153] In considering the relative merits of carbon monoxide and hydrogen in fuel gases the often objectionable effect of faster rate of combustion of hydrogen should be balanced against the better radiating power of its combustion product. Several books [154] have been published which discuss the combustion of gases.

SULFUR PRODUCERS

For several years an interesting process has been in operation on a large scale at Trail, B. C., in which producers are used for reduction of sulfur dioxide to sulfur. The thermodynamics of this process have been described by Lepsoe,[155] who has dealt with the kinetics in a second paper.[156] The investigation included the different possible side reactions and the use of different types of carbon, catalyzers, etc.

[152] Hottel, H. C., *Trans. Am. Inst. Chem. Engrs.*, **19**, 173–205 (1927).

[153] Wheeler, R. V., ref. 66.

[154] Haslam, R. T., and Russell, R. P., ref. 66. Perry, J. H., editor-in-chief, *Chemical Engineers' Handbook*, McGraw-Hill Book Co., New York, 1934, 2609 pp. Walker, W. H., Lewis, W. K., McAdams, W. H., and Gilliland, E. R., ref. 94. Segeler, C. G., editor, *Fuel Flue Gases*, American Gas Association, New York, 1940, 198 pp.

[155] Lepsoe, R., *Ind. Eng. Chem.*, **30**, 82–100 (1938).

[156] Lepsoe, R., *ibid.*, **32**, 910–8 (1940).

Lepsoe concluded that the principal reactions are:

$$SO_2 + C = CO_2 + \tfrac{1}{2}S_2$$

$$CO_2 + C = 2CO$$
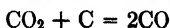
The rate of carbon dioxide formation between 900 and 1,200° C was in accord with the relationship

$$(CO_2) = 1.11\,[(SO_2)^{0.1} - SO_2]$$

the ratio between the apparent reaction constants for sulfur dioxide and carbon dioxide being 10 : 1. From the fact that sulfur dioxide is actually reduced at a rate only 5 times faster than the carbon dioxide reduction, it was concluded that a third reaction

$$SO_2 + 2CO = 2CO_2 + \tfrac{1}{2}S_2$$
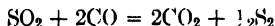
takes place as a first-order reaction at the coke surface with the ash acting as catalyst.

Above 1,200° C, the sulfur dioxide reduction is governed principally by gas diffusion, the same depth of fuel bed being required for sulfur dioxide reduction, regardless of gas velocity. Sulfur dioxide and carbon dioxide reduction parallel one another, since both reactions require oxygen to supply heat. The hot zone for sulfur dioxide reduction is greater than that for carbon dioxide, and its temperature should not be less than 1,300° C.

Reduction of sulfur dioxide by carbon monoxide or carbon oxysulfide is fast above 800° in the presence of catalyzing surfaces. At low temperatures (250 to 500° C), slightly hydrated acid-soluble alumina is an efficient catalyst, and the reaction is of the first order.

In the full-scale plant the process is conducted in 10-foot producer shells, using coke as fuel, and sulfur dioxide and air, if necessary enriched with oxygen, as blast.

The elemental sulfur formed in the reduction process is condensed from the final gases.

UNDERGROUND GASIFICATION

In the past the possibility of gasifying coal underground has occasionally been discussed, and among the earlier references may be mentioned a paper by Lanza.[157] Since 1933 the process has been seriously investigated and exploited by a special Russian government trust, Podzem. An extensive Russian literature has grown out of this work. A review of it in English appeared in 1936 by Chekin and associates.[158]

The simplest method with two holes, one for air-blast injection and one for gas extraction, was found to entail many difficulties. Successful results were obtained by the "mining method," in which shafts are sunk and sometimes an underground fuel bed is prepared. Obviously, the principal difficulty of any of these schemes is channeling, with subsequent carbon dioxide formation. Among the earlier methods is the one of Kirichenko, who prepared the coal bed with a series of dynamite-charged holes, the charges igniting successively and in this manner preparing the fuel bed as the fire approached. However, no regularity of operation could be established. The method of Kuznetzov calls for the preparation of the coal bed with a set of chambers (warehouse method) all connected in parallel to an inlet and outlet channel. The chambers were filled with crushed coal. The method was tried with indifferent success on a 0.45- to 0.5-meter anthracite bed; gas varying from 750 to 1,100 calories per cubic meter (78 to 115

[157] Lanza, L., *Fuel,* 1, 243–4 (1922).
[158] Chekin, P. A., Semenoff, A. I., and Galinker, I. S., *Colliery Guardian,* 162, 1193–6 (1936) ; *Fuel Economist,* 11, 331–5 (1936).

Btu per cubic foot) was made with carbon dioxide 12 to 18 percent, carbon monoxide 10 to 19 percent, hydrogen 6 to 12 percent, and methane 1 to 2 percent. The preparation of the bed is expensive. One large plant is said to be under construction.

Two more recent methods have shown more promise. One developed by Skaf and associates was tested out in the Donets Basin at Gorlovka. A coal bed was used containing 11,000 to 12,000 tons of gas coal (17 percent volatile matter) at a dip of 70°. The blast was introduced in one test pit while the gases were collected from another. A number of cross cuts were provided in the surrounding rock for access to the sidings in the coal bed. The coal was not crushed, and little timbering was provided. By this "stream method," using a blast containing 27 to 30 percent oxygen, a gas, 10 to 12 percent carbon dioxide, 23 to 27 percent carbon monoxide, 12 to 15 percent hydrogen, 2 to 3 percent methane, 43 to 47 percent nitrogen, and 1,000 to 1,300 calories per cubic meter (104 to 136 Btu per cubic foot), was made with great regularity. The oxygen content of the blast controlled the gas composition. When the blow was interrupted, a gas containing 60 to 70 percent hydrogen and 15 percent nitrogen was developed which was attributed to diffusion into and out of the surrounding rock. This gas was suitable for chemical synthesis. Operating the Gorlovka mine on periodical blast, there were made per 24 hours 25,000 to 30,000 cubic meters of power gas (carbon dioxide 18 percent, carbon monoxide 15 percent, hydrogen 20 percent, methane 3 percent, nitrogen 44 percent, 1,225 calories per cubic meter [128 Btu per cubic foot]) and 12,000 to 15,000 cubic meters of chemical gas. The blow periods varied from 4 to 6 hours. With 35 percent oxygen in the blast, a gas

has been made containing 18 percent carbon dioxide, 15 percent carbon monoxide, 49 percent hydrogen, 4 percent methane, and 14 percent nitrogen, which is as good as gas from an ordinary producer with 60 percent oxygen in the blast. The results of "stream" gasification with air are less promising, although a 800- to 1,000-calorie (83- to 104-Btu) gas has been made by Grindler.

In horizontal beds (no dip) such as those of the Kuznetz Basin there has been more trouble with the roof caving in and blocking gas flow. One method for remedying these difficulties, proposed by Semenoff and Galinker, was the use of an alternate blow of steam and air (or oxygen). This procedure did not require uniformity in the fuel bed ("regenerative method"), and a species of blue water gas was thus made. Anthracite model experiments yielded a gas containing 15 percent carbon dioxide, 0.5 percent oxygen, 26 percent carbon monoxide, 53 percent hydrogen, and 0.7 percent methane. Construction of five or six plants was said to be started on the stream and regenerative systems. German articles by Gumz [159] on underground gasification, which reviewed the developments of the Russian technique, stated: "Underground gasification is possible technically and economically, mining labor is reduced to a minimum." A description was given in detail of the stream process and of a modification in which a blast was introduced on two sides of a part of a coal seam with steep dip and gas was extracted in the center; danger of the zone's spreading was thus limited. A slight suction was maintained on the gas outlet. The fire proceeded from the bottom of the seam parallel to the strike. Owing to the dip, falling rock did not obstruct the flow of

[159] Gumz, W., *Glückauf*, **76**, 210–13 (1940); *Feuerungstech.*, **28**, 56–9 (1940).

gases. Besides five experimental plants there is one industrial plant (Gorlovka). The experimental unit at the same location produced (1938) in one and a half years of uninterrupted operation 7 million cubic meters of power gas of 1,100 calories per

FIG. 24. Volume, heating value, and composition of gases recovered from underground gasification of coal at Gorlovka.[159]

cubic meter (115 Btu per cubic foot), and 2 million cubic meters of chemical gas of 2,000 calories per cubic meter (210 Btu per cubic foot). The coal seam was 1.9 meter thick with a 70 to 75° dip. The composition and quality of the gases obtained by intermittent flow are shown in Fig. 24.

In a still more recent process reported on by Gumz[160] a number of holes were drilled in the coal field. The fire was started with a double tube in the center

160 Gumz, W., *Glückauf*, **76**, 670–2 (1940).

hole. Eventually this hole served as inlet for the blast; other holes surrounding it in a circle, as gas outlet means.

Chukhanov[161] has reported on the regulation of temperature in subterranean gasification.

APPLICATIONS OF PRODUCER GAS

INDUSTRIAL HEATING

Gaseous fuel is preferred for all industrial heating processes where the control of combustion is of prime importance and where direct firing with modern types of solid-fuel combustion units is impractical. Producer gas has been among the most popular types of gaseous fuel since it can be made in a continuous process, requiring little supervision, from low-grade solid fuels. It is in competition with other gaseous fuels such as natural gas and blast-furnace gas, and with liquid fuels like tar and fuel oil.

Distinction must be made between two types of application of producer gas. In the one the gas is used hot and without purification; open-hearth furnaces are an example. In the other the gas is cleaned (tar and dust removed), and at the same time the gas temperature is reduced; coke ovens are examples. Use of hot, uncleaned gas is preferable from the point of view of heat utilization. The sensible heat of the gas is utilized, and the tar, partly in vapor form and partly suspended in the gas, is burnt up with direct recovery of its heat value. In this manner the first cost of cleaning and cooling installations is avoided and preheating of the gas in regenerators is partially or completely avoided. The principal drawbacks of this type of gas utilization are rapid contamination of pipe lines, which should preferably be short,

161 Chukhanov, Z. F., *Compt. rend. acad. sci. U.R.S.S.*, **27**, 203–8 (1940) (in French).

contamination of direct-fired products such as glass and ceramic ware by the precipitation of suspended ashes on it, sulfur con-

FIG. 25.   Siemens producer with step grate. After Rambush.[66]

A = fuel hopper.
B = sloped side.
C = grate bars.
D = gas offtake.
E = poke hole.
F = water spray pipe.

tamination of the products by the impurities in the gas, and deposition of ashes in regenerators.

Cleaned gas lacks these objectionable features, and its use has increased. It should be realized, however, that although cleaning is feasible for gases derived from any type of fuel a rather elaborate installation is required for the gas from fuels of high volatile content (bituminous coal, wood, etc.). The removal of small amounts of tar fog is among the most difficult cleaning problems. By preference, therefore, fuels of low volatile matter (anthracite, coke) are used in the manufacture of cold, clean producer gas. Adequate cleaning of hot gas without cooling has as yet not proved feasible. Certain kinds of producers such as the double-draft type are designed to decompose the tar derived from volatile matter by contact with the incandescent portions of the fuel bed.

FIG. 26.   Glover-West step-grate producer with pressure equipment.

Among the literature pertinent to the application of producer gas to steelworks practice, an exhaustive study of Husson [162] was concerned with the characteristics of producer gas required for use in open hearths. The effect of volatile matter in

A = Fuel Bed
B = Hopper
C = Gas Offtake
G = Grate
H = Ash Pan
D = Water Jacket
F = Poke Holes

FIG. 27. Pierson suction gas producer. After Rambush.[66]

the coal upon the quality of the resulting gas was studied. Slottman [163] discussed the status of the gas producer in the iron and steel industry, as also have Luth and Le Châtelier.[164] Suggestions for the use

of oxygen-enriched air in making producer gas for open-hearth furnaces have been made by Nagle.[165]

The qualities of producer gas and its use in glass furnaces have been discussed by several authors.[166] The possibilities of substituting clean producer gas for city gas in different glassworks applications were pointed out. The suitability of coals for use in glassworks producers was reviewed in some detail by Sismey.[167] The qualities of coals desirable for built-in as well as for mechanical producers were discussed, including the effect of size, hardness, volatile-matter content, caking tendency, ash content, sulfur content, chloride content, and calorific value.

The use of producer gas for underfiring of coke-oven batteries and gasworks furnaces has been discussed by several authorities.[168] Its outstanding advantage is the economic utilization of the smaller sizes of coke, unsuited for domestic or industrial markets.

POWER

The use of producer gas in combustion engines is relatively old. The overall effi-

[162] Husson, G., *Rev. ind. minérale*, **2**, 373–406 (1922).

[163] Slottman, G. V., *Proc. 3rd Intern. Conf. Bituminous Coal*, **1**, 866–73 (1931).

[164] Luth, F., *Stahl u. Eisen*, **52**, 1213-21 (1932). Le Châteller, C., *Chimie & industrie*, **37**, 835–51 (1937).

[165] Nagle, T., *Am. Inst. Min. Met. Engrs., Contrib.* **100** (1936), 5 pp.

[166] Windett, V., *Proc. Engrs. Soc. West. Penna.*, **44**, 11–46 (1928). Romig, J. W., *Glass Ind.*, **10**, 283–5 (1929), **11**, 1–3, 30–1, 62–3, 80–1, 179–81 (1930). Hurlbut, F. J., *J. Soc. Glass Tech.*, **19**, 330–8 (1935). Knapp, O., *Glashutte*, **65**, 561–4 (1935), **68**, 553–6, 579–80 (1938). Gauger, A. W., *Bull. Am. Ceram. Soc.*, **19**, 365–8 (1940).

[167] Sismey, D., *J. Soc. Glass Tech.*, **21**, 215–31 (1937).

[168] Rambush, N. E., and Townend, F. S., *Trans. 2nd World Power Conf., Berlin*, **2**, 165–75 (1930). Hilgenstock, P., *Glückauf*, **67**, 1199–203 (1931). Kellner, F., *ibid.*, **68**, 1165–73 (1932). Kircher, A., *Bergbau*, **1935**, 328–9. Dinsdale, C., and Curtis, E. A., *Colliery Guardian*, **152**, 160–2, 201–2 (1936). Drury, P. G., *Gas World*, **104**, Coking Sect. 16–24 (1936), **109**, Coking Sect. 89–90 (1938); *Colliery Guardian*, **157**, 329–31 (1938).
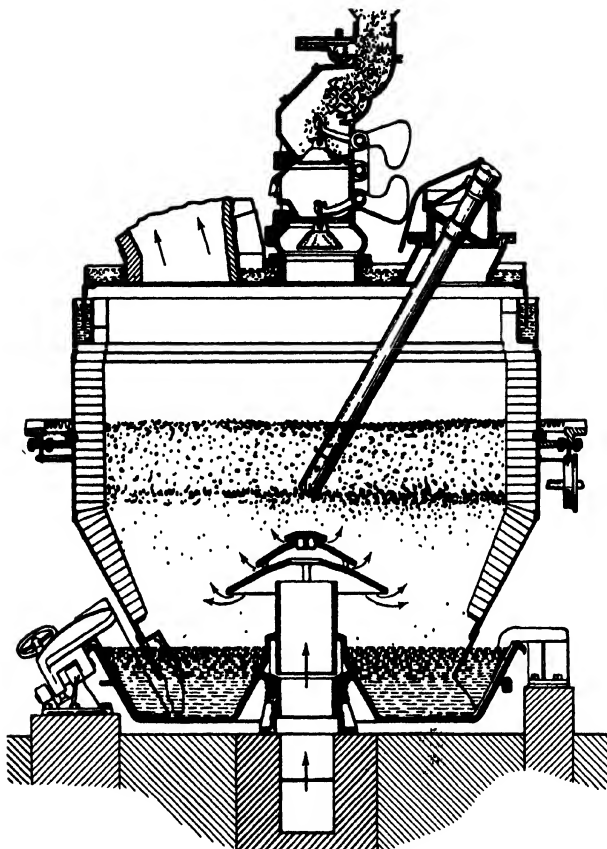
FIG. 28.   Wellman-Seaver-Morgan gas producer using coal.

ciency of the conversion of chemical energy of the fuel to mechanical energy of the engine is fairly good for the combination producer-gas engine; its first cost and supervision cost are moderate compared with those of a boiler-steam engine installation, especially for a small-scale plant. With the advent of the more modern types of stokers for cheap boiler fuel, of natural gas, and especially with the prevailing low prices and availability of fuel oil for Diesel engines, power producers have become rare.

Economic conditions abroad, being radically different from the standpoint of fuel availability, have forced a development in the opposite direction, and a veritable revival of power producers has taken place in England, France, and Germany. These producers are meant to be used principally as individual, small units, on automotive vehicles, especially trucks, and to eliminate the use of gasoline. It is obvious that producer gas for a gas engine should be cold and clean, and a number of ingenious
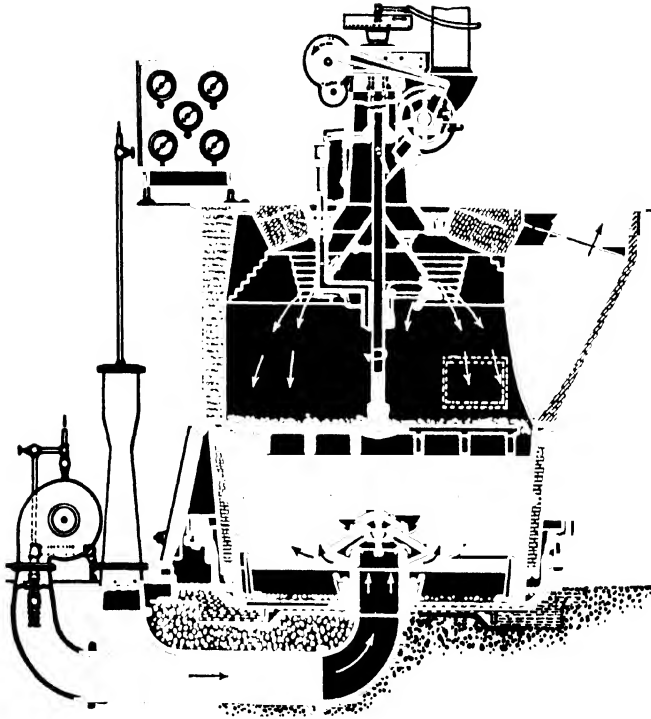
FIG. 29. Chapman gas producer.

cleaning devices for this purpose have been built. A number of excellent reviews have been published on this late development of the power producer, outstanding among which is a paper by Goldman and Clarke-Jones,[169] who covered the field in very satisfactory manner and gave a large number of references. Other notable papers dealing with these developments are by Hartner-Seberich, Berthelot, Brückner, and Finkbeiner.[170]

Fuels for vehicle producers have been discussed by several investigators.[171] Rasch [172] discussed especially the clinker problem of vehicular producers. A number of pamphlets also have appeared dealing with vehicular producers.[173]

[169] Goldman, B., and Clarke-Jones, N., *J. Inst. Fuel,* **12,** 103–40 (1939).

[170] Hartner-Seberich, R., *Brennstoff-Chem.,* **17,** 1–11 (1936); *Fuel,* **16,** 15–27 (1937). Berthelot, C., *Génie civil,* **110,** 376–8 (1937). Brückner, H., *Gas- u. Wasserfach,* **80,** 446–51, 463–6 (1937). Finkbeiner, H., *Feuerungstech.,* **26,** 106–9 (1939).

[171] Smith, D. J., *Proc. Inst. Automobile Engrs.,* **14,** 169–239 (1920); *Engineering,* **109,** 59–64, 92–5 (1920). Berthelot, C., *Chimie & industrie,* **34,** 759–62 (1935). Schultes, W., *Brennstoff-Chem.,* **17,** 61–7 (1936). Gevers-Orban, E., *Rev. universelle mines,* **13,** 249–59 (1937). Linneborn, H., et al., *Automobiltech. Z.,* **40,** 449–68 (1937).

[172] Rasch, R., *Glückauf,* **75,** 239–42 (1939).

[173] *Gas Producers for Motor Vehicles, Their Design and Operation,* Science Library, Bibliographical Series **415,** London, 1938, 8 pp. (161 references 1930–1938). Petit, H., *Les véhicules à gazogène,* Dunod, Paris, 1938, 75 pp. Rouyer,
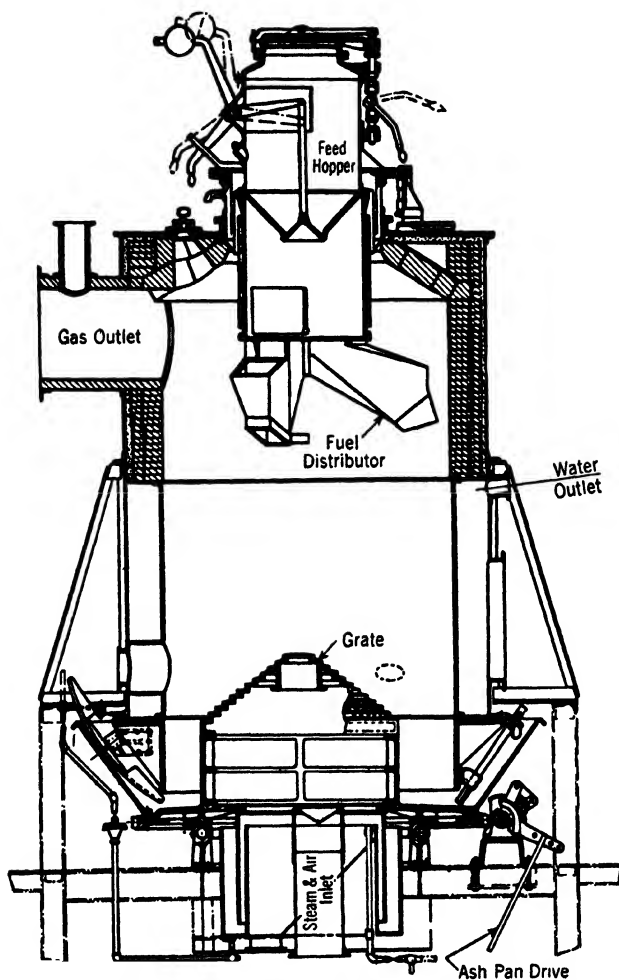
Fig. 30. Koppers-Kerpely gas producer with coke distributor, revolving grate, and ashpan.

By special procedures, gases different from common producer gas can be made by continuous complete gasification of different fuels. For the purpose of synthesis of hydrocarbons by the Fischer-Tropsch process a gas containing 1 volume of carbon monoxide to 2 volumes of hydrogen is required. Several continuous processes are able to meet this requirement. Similar processes are used to produce gases of high heating value suitable as city gas.

CLASSIFICATION OF PRODUCERS

USUAL CONSTRUCTIONS

Blast and Fuel Travel. One customary distinction in producer classification is determined by the direction of travel of the blast and the fuel. The simplest and commonest type of producer with fuel travel downward and blast upward is the *up-draft* producer. Ash is removed from the bottom of the fuel bed, gas from the top. The gas contains the distillate from the volatile matter of the fuel in a slightly decomposed form. In the *down-draft* producer the direction of the blast travel as well as that of the fuel is downward. The volatile matter is more completely decomposed by forcing all the gases through the hot zone. This type of producer is not used to an appreciable extent. The *cross-draft* producer with the introduction of the blast on one side with practically horizontal travel of blast across the fire bed to the gas outlet on the other side, and fuel travel

G., *Étude des gazogènes portatifs,* Dunod, Paris, 1938, 75 pp. Finkbeiner, H., *Hochleistungs-Gaserzeuger fur Fahrzeugbetrieb und ortsfeste Kleinanlagen,* J. Springer, Berlin, 1938, 99 pp. Heywood, H., and Rose, H. E., *British Coal Utilization Research Assoc.,* Doc. C/446 (1939), 35 pp. Hartley, H., Chairman, *Report of the Committee on the Emergency Conversion of Motor Vehicles to Producer Gas,* Mines Dept. (Brit.), London, 1940, 27 pp.

downward, has become popular for small-scale, high-speed vehicular producers. An additional, relatively rare type is the *double-draft producer,* in which the blast
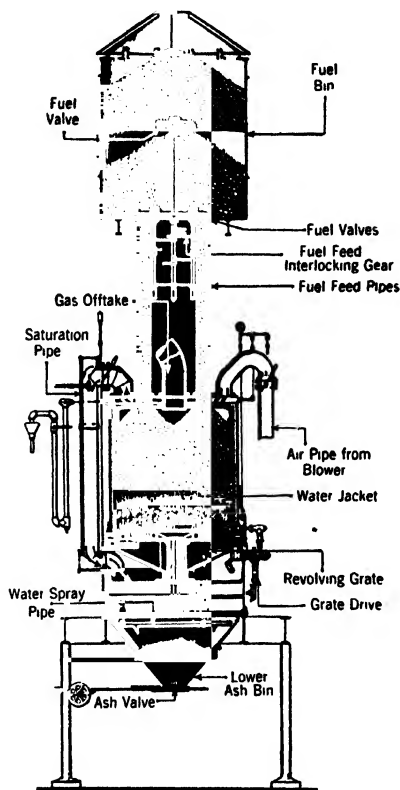
FIG. 31. Wellman Galusha gas producer.

enters from above as well as from below. It has several features of the down-draft producers.

Pressure Conditions. Atmospheric (or balanced-draft) producers operate under pressures substantially atmospheric. In order to overcome the resistance of the fuel bed to the blast, air blowers or injectors

FIG. 32. Dowson double zone suction gas producer using bituminous coal   After Rambush [66]

Preheater and
Dust Separator

Plan of Tuyeres
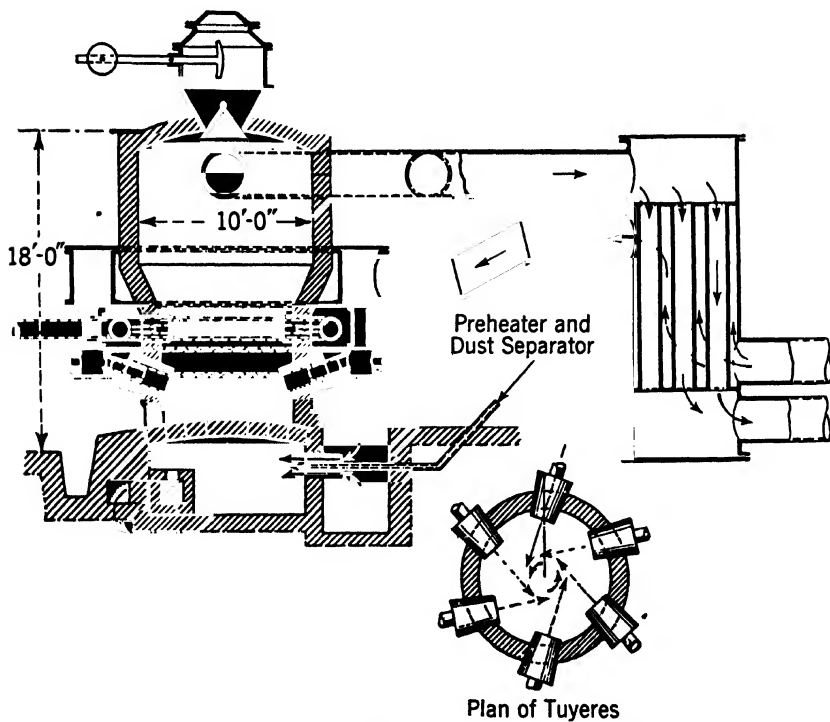
FIG 33. Wuerth's liquid slag gas producer. After Rambush [66]
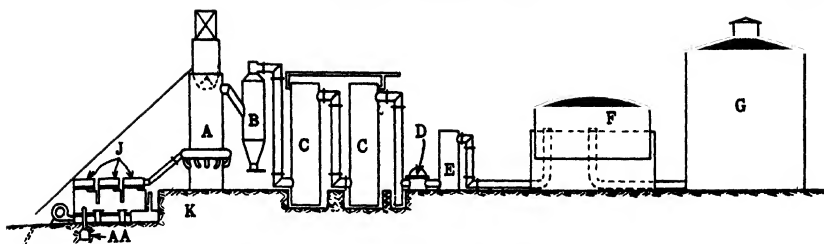
FIG. 34. Phillipon slagging producer plant.

A = gas producer.
B = dust catcher.
C = scrubbers.
D = disintegrators.
E = water separator.
F-G = gas holders.
J = air preheaters.
K = gas burners.
AA = waste-gas duct.

are needed to operate such producers; if the gases are to be used at some distance away from the producer, boosters are employed occasionally for gas transmission. This type of producer is safe from the supplied the suction required to force the blast through the fuel bed. It is obvious that this type of producer cannot work with very high blast rates and is therefore limited in capacity. The brick shaft
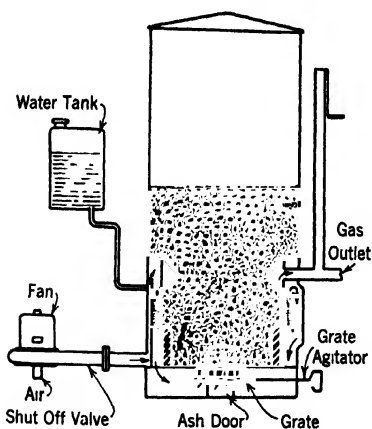
FIG. 35. Wisco gas producer.[169]
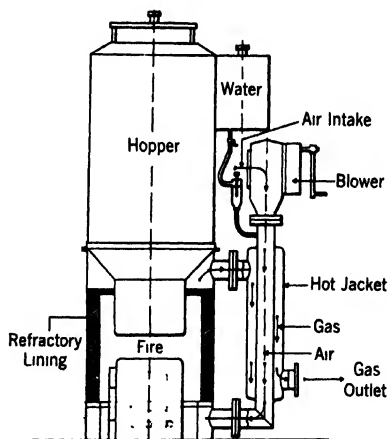
FIG. 36. Koela up-draft gas producer.

point of view of gas leakage and control and is by far the most common. The gas pressure at the top of the producer is usually slightly positive, from 1 to 5 inches water column.

Suction producers were often used in the manufacture of power gas; the gas engine

producers often of the so-called built-in type, found in gasworks, are usually suction producers.

Pressure producers serve special purposes where gases other than ordinary producer gas are desired. High pressure is extremely desirable for the production of

gases having a high methane content. Pressure producers are totally enclosed and sealed.

Ash Removal. The original Siemens producer had a stationary grate and fire door. At definite intervals ash and clinker were eliminated by *hand removal.* Such
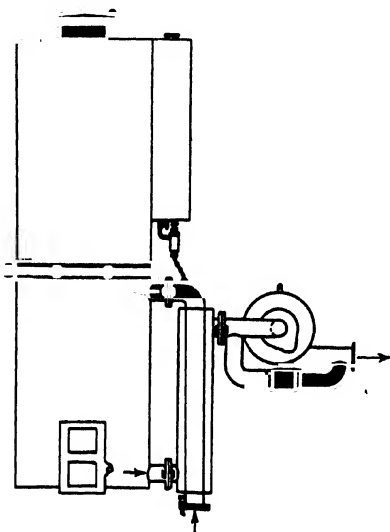
FIG. 37.   Koela down-draft gas producer.[169]

FIG. 38.   Gohin-Poulenc gas producer.[169]

itself up according to its angle of repose. By rotating either the shell or pan and placing an obstruction (plow) in the path of the ash the angle of repose is disturbed, the ash builds up in front of the obstruction and is removed by spilling over the edge of the pan or by digging it out of the pan. Most modern producers have this type of *mechanical ash removal.*

A radically different type of ash removal determined by the difference in the

interruptions in operation meant loss of efficiency. Later types of hand-operated cylindrical producers removed ash from the periphery of the cylinder which was set up in a circular pan. For higher operating rates, it was necessary to introduce the blast under pressure, and naturally the old ash-removal systems had to be modified. The producer shell was sealed either by boxing it in (dry seal) or by placing it in a water-filled pan (water seal). Later the ash removal in such producers was usually made automatic by rotating either the producer shell or the seal pan. The ash normally flows out of the shell and sets

FIG. 39.   HSG gas producer.[169]

operation of the producer is the *slagging producer*. As in a cupola or blast furnace, the ash in this type of producer is allowed to melt and is collected in the liquid state in the hearth of the producer. It is removed by tapping at set intervals, or sometimes it is permitted to cool and removed as a solid ball of clinker.

A third method of ash removal is to carry it away with the gases and to collect it in dust pockets provided in the gas lines. This procedure is followed in part in a number of high-speed producers.

Blast Introduction. In up-draft producers the blast is usually introduced under pressure. Whereas the older types of producers had flat, inclined, or stepped bar grates, the newer units have conical-shaped grates fabricated from either flat plates with spacers or castings with rows of holes. Sometimes the grate is shaped like a mushroom. The blast enters through the hollow center of such a grate and is distributed through the holes or slots into the fuel bed somewhere near the center of the producer. It is advantageous to do this since the gases have a natural tendency to rise up along the walls. Usually the desired quantities of steam are added to the air blast underneath the grate. In slagging producers the high-velocity blast is introduced through cooled tuyères situated in the side walls of the producer.

Fuel Feed. Up-draft producers in the simple form are fed intermittently by dropping hopper loads of fuel into them, the fuel being distributed evenly over the bed by means of simple baffling devices and variously shaped "bells." An improved type of feed found in many mechanical producers is a magazine feed which automatically maintains the fuel bed at the desired level. Ring feed, pantsleg feed, and similar designations are applied to this apparatus. Some of these feed devices will

exert at the same time a leveling effect on the top of the fuel bed. Simple stationary magazines with pipes reaching down to the fuel bed are likewise in frequent use. For

FIG. 40. Lurgi gas producer for high-pressure oxygen-blast operation. After Danulat.[114]

fuels having high volatile-matter content magazine feeds are less popular because of precarbonization difficulties in the magazine. For special fuels, a more complicated feeding arrangement such as a worm feed may be found necessary.

Stirring Devices. In order to maintain the fuel bed of the up-draft producer in

uniform physical condition stirring is often applied from below or above. In general, in mechanical producers it is applied from below. The rotation of the pan or shell creates an agitating effect, especially if the grate cone is slightly offset from the center line of the producer or if stirring devices are attached to the grate. Stirring from the top of the fuel bed is applied for fuels like bituminous coal that tend to cake. It is necessary to loosen the cake continuously, in order to prevent channeling of the blast, by means of cooled poker bars, raking devices, or similar apparatus.

Shell Construction. Built-in producers are constructed as a square firebrick shell with a magazine-type feed. Practically all other producers are built as cylindrical steel shells. For protection against heat such shells are either lined with fireclay brick or backed up with a water jacket. With a water jacket, low-pressure and sometimes high-pressure steam is frequently produced. The walls of the clay-lined producers should be kept relatively cool to avoid the formation of "wall clinker." Sometimes plain steel shells are used for small producers in which the fire zone is in the center of the charge (as in the cross-
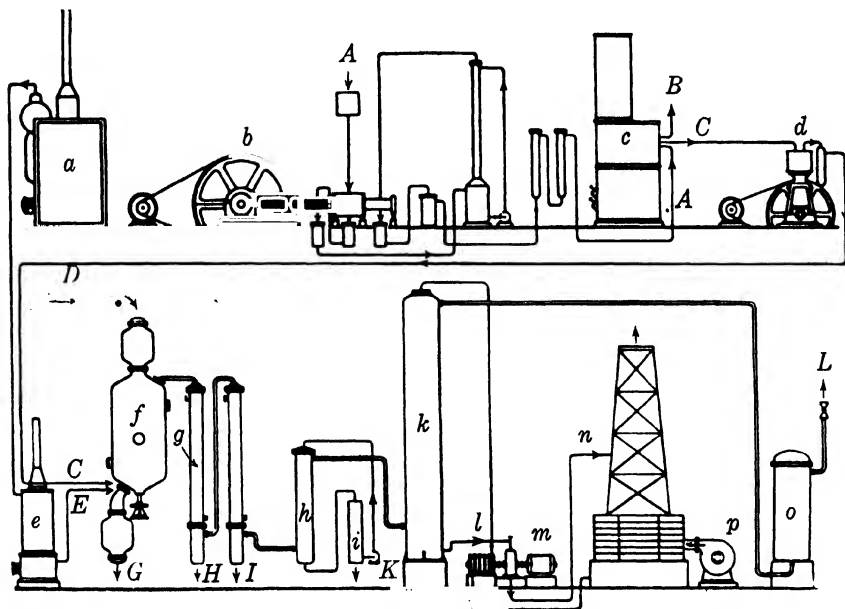
FIG. 41. Lurgi gas producer plant for operation with oxygen under pressure. After Danulat.[114]

A = air.	G = ash.	a = steam boiler.	i = stripping apparatus.
B = nitrogen.	H = tar.	b = air compressor.	k = pressure water wash.
C = oxygen.	I = middle oil.	c = separator.	l = pump.
D = fuel.	K = benzine.	d = oxygen compressor.	m = turbine.
E = steam.	L = pure gas.	e = steam superheater.	n = aeration tower.
F = crude gas.		f = gas producer	o = extraction of sulfur
		g = cooler.	residue.
		h = benzine scrubber.	p = air blower.

draft producer) and separated from the walls by unconsumed fuel.

MISCELLANEOUS CONSTRUCTIONS

Hand-Operated Producers. As shown in Figs. 25 and 26, this simple type of producer is essentially a brick shaft, part of which constitutes the fuel magazine, and a flat or step grate. It is often built integrally with the furnace to be fired, hence the designation "built-in" producer. This producer is hand-ashed and frequently hand-fed. Occasionally the grate is sealed and pressure blast used, but the unit is customarily operated under a suction. A fairly large number of these producers are in operation. Their characteristics, operation, and results have been described frequently.[174] The throughput of these producers is 10 pounds of fuel per square foot per hour or less, and quite often the gas quality is erratic. Rambush has described at some length a number of producers in this classification.[66]

From the simple square brick shell, there is a gradual transition to the cylindrical steel-shell, brick-lined producer with the several types of blast introduction. An example of a small suction producer unit is shown in Fig. 27; it is hand-ashed and magazine-fed. This type of producer, intended to provide gaseous fuel in connection with a gas engine, is suction operated and usually of up-draft type. It is the prototype of modern vehicular producers.

Mechanically Operated Producers. Up-Draft: Among the more common producers of this class for coal are the Wellman, Chapman, Morgan, and Wood producers (Figs. 28 and 29), which are provided with
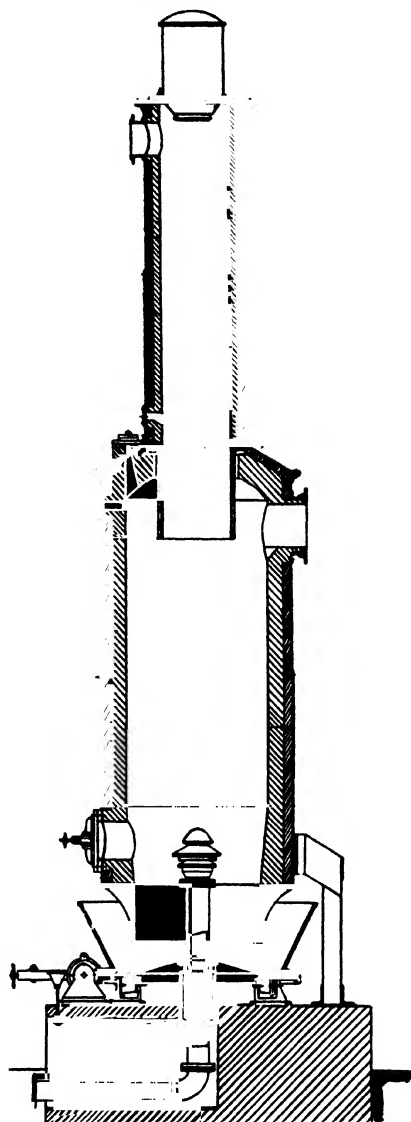
Fig. 42. Drawe gas producer for operation with oxygen at atmospheric pressure.[117]

[174] Kennedy, F. J., *Am. Gas J.*, **133**, No. 1, 50-2, 57 (1930). Haug, J. S., *Proc. Am. Gas Assoc.*, **1930**, 970-6. Smith, E. W., *Gas J.*, **196**, 204-7 (1931). Dubois, E., and Schmid, J., *Gas- u. Wasserfach*, **75**, 921-6 (1932); *Gas J.*, **200**, 694 (1937). Stadler, O., *Schweiz. ver. Gas- u. Wasserfach., Monats-Bull.*, **16**, 25-35 (1936); *J. usines gaz*, **60**, 528-88 (1936).

stirring devices, revolving central grate or shell, brick lining with or without jacket, mechanical fuel feed, and pressure blast. Producers of this type for use with coke or anthracite as fuel are the Koppers-Kerpely, U.G.I., Koller, and Galusha (Figs. 30 and 31), usually without an upper stirring device and provided with a low-pressure steam jacket. These units have mechanical ash-removal mechanism, magazine fuel feed, revolving central grate, and pressure blast. There is considerable variety in detail of construction of these producers.

The Trefois producer has been described by Holton,[175] the Sauvageot producer by Delot and others; [176] articles have also

been published which have described the Heurtey producer,[177] the "ash crusher producer," [178] the high-pressure steam jacket producer, including the Marischka and Pintsch types,[179] the Schwaller,[180] the Galusha,[181] and the Koller [182] producers.

The more common types of producers of this class are amply described in all standard textbooks. The maximum rates of

(1930) ; *Stahl u. Eisen*, **50,** 1376 (1930). Anon., *Chaleur et ind.*, **14,** 824–5 (1933).

[177] Anon., *Génie civil*, **98,** 403–4 (1931).

[178] Anon., *Chaleur et ind.*, **12,** 258–60 (1931). Caldier, M., *ibid.*, **13,** 132–6 (1932).

[179] Mezger, R., Kratsch, H., and Baum, K., *Gas- u. Wasserfach*, **75,** 825-30 (1932). Hecker, E., *ibid.*, **75,** 329–35 (1932).

[180] Schwaller, F., *Verre silicates ind.*, **7,** 142–4 (1936).

[181] Anon., *Fuel Economist*, **5,** 619–20 (1930) ; *Iron & Coal Trades Rev.*, **122,** 318–9 (1931).

[182] Anon., *Iron & Coal Trades Rev.*, **123,** 232 (1931).

[175] Holton, A. L., and Applebee, H. C., *Gas J.*, **192,** 150–6 (1930) ; *Gas World*, **93,** 340–6 (1930). Holton, A. L., *Coke*, **1,** 201–2 (1939).

[176] Delot, M., *Aciers spéciaux*, **3,** 568–74
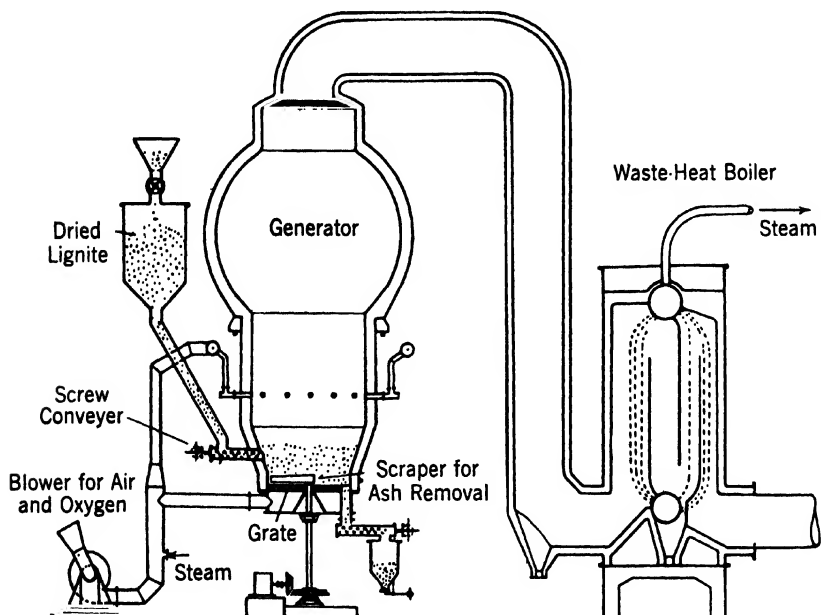
Fig. 43. Winkler gas producer for operation with oxygen under pressure.[115]

gasification for producers in this class are normally in the neighborhood of 60 pounds per square foot per hour, but results as high as 100 pounds per square foot per hour have been reported. The average size of this type of producer is 7 to 12 feet width, with a fuel-bed height 2 to 6 feet. For constructional details the literature should be consulted. This type of generator is in use for making hot uncleaned gas from high-volatile-matter fuels as well as for making cold clean gas. Most of the processes for making special gases by complete gasification are of the updraft mechanical type and will be discussed later.

Down-Draft and Double-Draft: Relatively few producers of this type are now in common use except as small units on motor vehicles. Rambush [66] quoted from a Canadian work [183] on various producers: "The combustion on the down-draft principle in the upper zones has many drawbacks and should be used only when it is not feasible to employ an up-draft producer requiring an elaborate external plant for removing the tar from the gas." The thermal efficiency of this type of plant appears to be relatively low. Likewise work by Fernald [184] indicated lower heating value of the (coal) producer gas from down-draft producers with no significant increase in gas volume. It is evident that the cold efficiency is low, probably because of increased gas outlet temperatures.

An example of a double-draft producer plant is shown in Fig. 32. Down-draft producers of the suction as well as the atmospheric type have been built. Doubledraft producers in which the air blast moves from the top of the fuel bed down

as well as from the bottom of the fuel bed up should not be confused with the "double-gas" type of generators, which make water gas in an intermittent process.

Slagging Producers. Slagging producers have been discussed previously; typical examples are shown in Figs. 33 and 34. Their throughput is high; figures of 700 pounds per square foot hour have been reported. Usually the hearth of these producers has iron as well as slag tapping notches, and the air blast is preheated. Several types of slagging producers have been described in detail by Rambush.[66]

Vehicular Producers. Goldman and Clarke-Jones [169] pointed out that up-draft, down-draft, double-draft, as well as crossdraft producers are used in generating fuel gas for vehicle engines.

Among the up-draft producers should be mentioned the German Wisco, Hansa, and Humboldt-Deutz, the British Koela, the Italian Dux, and the French Malbay and CGB types. They yield the best-grade gas but are subject to tar troubles; the preferred fuels in these units are low-temperature coke, anthracite, charcoal, or charcoal briquets. Steam is normally used in the blast. Figure 35 shows the Wisco producer.

Down-draft producers include the British Koela, Italian Fiat, German Imbert, Swedish Svedlund and Graham-Stedts, and French Imbert, Panhard, Sabatier, Sagam, Guillaume, and Rustic types. The gas made is of lower quality but the tar is destroyed. Usually no water vapor is used in the blast. Preferred fuels are charcoal, or charcoal briquets, wood, and other tarry fuels. Figures 36 and 37 show a type of producer which can be used for either up- or down-draft operation.

Double-draft types are the French Brandt and the British Koela producer.

183 Blizzard, J., and Malloch, E. S., *Can. Dept. Mines, Bull.* **33** (1921), 40 pp.
184 Fernald, R. H., *U. S. Bur. Mines, Bull.* **109** (1915), 74 pp.

A novel producer hitherto used only as a vehicular unit is the cross-draft type. Figures 38 and 39 are typical examples of this construction. A water-cooled tuyère inserted inside the shell almost to the center of the charge serves as the air inlet with or without moisture addition to the blast. The gas leaves at the opposite side of the shell. Producers of this type are the French Gohin-Poulenc (the original one) and Dupuy, British HSG, and Belgian Bellay. Charcoal, low-temperature
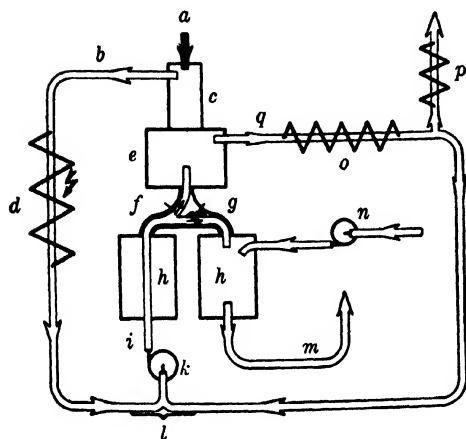
a – Lignite Briquets
b - Low Temperature Carbonization
      Gas and Recirculated Gas
c - Low Temperature Carbon Shaft
d – Electrical Tar Precipitator
e – Gasification Shaft
f – Recirculated Gas
g – Heating Gas
h – Regenerator
i – Recirculated Gas and Heating Gas
k – Recirculated Gas Blower
l – Recirculated Gas and Heating Gas
m – Waste Gas
n – Air Blower
o – Gas Scrubber and Water Evaporator
p – Cooler for Production Gas
q – Gas Make
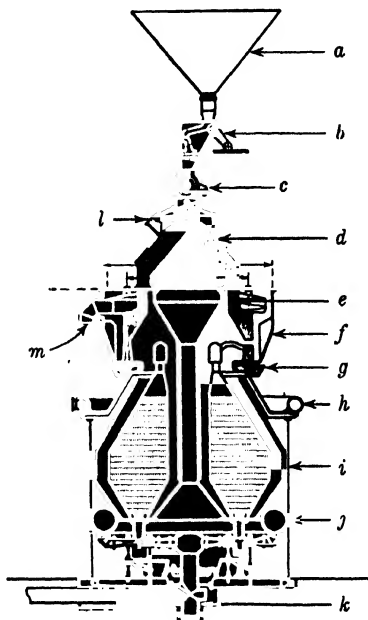
a – Briquet Hopper
b – Automatic Scale
c – Automatic Feeder
d – Coal Distributor
e – Low Temperature Carbonization Shaft
f – Gasification Shaft
g – Ash Removal
h – Circular Blast Pipe
i – Regenerator
j – Recirculated Gas Header
k – Waste Gas Pipe
l – Low Temperature Gas and
      Recirculated Gas
m – Gas Make

FIG. 44. Pintsch-Hillebrand gas producer with recirculation.

coke, anthracite, or mixed fuels are preferred fuels. The fuel should be fairly reactive. The ash is removed as a fused ball. Easy starting is claimed as an advantage for this type of apparatus. Since the extremely hot fire zone is in the middle of the charge, the walls of this producer do not require lining. Variations of this producer type preheat the blast (Bellay). The Gohin type of vehicular producer seems the most practical and efficient unit. All vehicular producers are hand-charged and hand-ashed.

Special Producers. For operation with oxygen there has previously been described the *Lurgi* producer, shown in Figs. 40 and 41. It can operate under pressure. The unit has a rotating grate and a water jacket (3 meters high) and is about 1 square meter in cross-sectional area. An earlier type of oxygen-blast producer (Drawe) is shown in Fig. 42. It operates under atmospheric pressure.

The *Winkler* producer, Fig. 43, also operating under pressure, works by preference on pulverized lignite which remains in suspension due to high blast velocities. Ash is removed by a wiper revolving over the flat grate, while part of the ash is entrained with the gas and removed from the large dustlegs following the producer. The fuel is introduced by a screw conveyor. The shaft area of the Winkler apparatus is about 20 square meters.

The *Pintsch-Hillebrand* generator, Fig. 44, has a pair of regenerators underneath the gasification and carbonization chamber.

The *Thyssen-Galoczy* gas producer, Fig. 45, operates with oxygen blast and slagging ash removal.

The construction of these various producer types is obvious from the illustrations. For detailed descriptions the literature should be consulted.

OPERATING RESULTS

In previous chapters operating results of some of the special types of producers, such as oxygen-blown, slagging, and under-
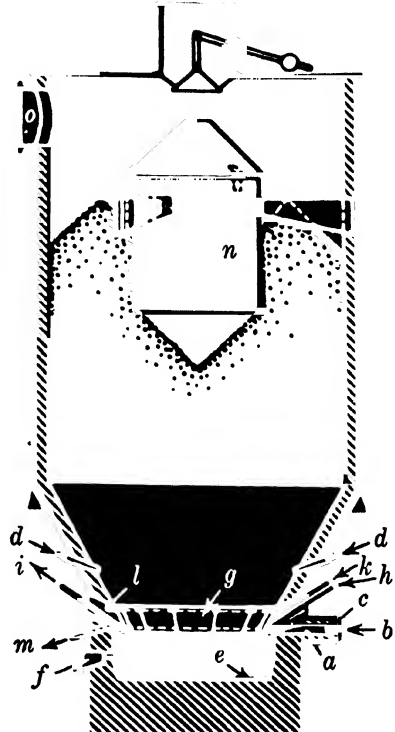
FIG. 45. Thyssen-Galoczy gas producer for slagging operation and oxygen blast.[121]

a = combustion chambers all around the producer.

b = inlet for oxygen saturated with water vapor.

c = inlet for auxiliary fuel gas

d = inlet for secondary oxygen or steam.

e = iron notch.

f = slag notch.

g = replaceable cooling jacket.

h-k = water inlets to jacket.

i = water outlet from jacket.

l = spray for outside cooling of jacket.

m = water outlet.

n = gas outlet pipe.

o = gas outlet.

ground, have been dealt with briefly. Such data are rather scarce. Abundant information is available in the literature on operating results of the more common types of producers, particularly of large up-draft and small vehicular ones. Elaborate reviews of producer practices and general discussions of the producer process have been given by a number of authors.[185] Heat balances and test data on large up-draft producers are given by several others.[186] Standards for testing gas producers have been set up by the American Gas Association and by the American Society of Mechanical Engineers,[187] also by different German and Dutch associations.[188] Standards of testing have been discussed also in several papers.[189]

The results obtained with different fuels, especially coal, in up-draft producers, are the subject of many papers[190] in which the effect of fuel composition on the gas is discussed. The use of small coke (breeze) in producers has been given special attention.[191] European literature abounds with information relative to the use of low-grade and special fuels, such as wood, lignite, lignite briquets, lignite coke, and low-temperature coke, in producers.[192]

A few typical operating figures on large mechanical up-draft producers using coal or coke are given in Table V. Typical heat balances of a coal producer making hot uncleaned gas and of a coke producer making cold clean gas are given in Table VI. Useful performance data on the operation of vehicular producers are given by Goldman and Clarke-Jones,[169] a part of which is condensed in Table VII.

[185] Dyrssen, W., *Yearbook Am. Iron Steel Inst.*, **13**, 96–162 (1923). Denig, F., *Proc. Am. Gas Assoc.*, **1927**, 1210–35. Chapman, W. R., *Trans. World Power Conf., London*, **2**, 1335–54 (1928). Demorest, D. J., *Fuels and Furnaces*, **7**, 1679 (1929), **8**, 235–8, 349–52 (1930). Wilson, L. J., *Fuel*, **9**, 152–64 (1930). Romig, J. W., *Am. Gas J.*, **133**, 47–8, 54–5 (1930). Slottman, G. V., *Proc. Am. Gas Assoc.*, **1930**, 978–85. Taylor, F. J., *Iron & Steel Industry*, **4**, 191–3, 339–42, 371–4 (1931). Windett, V., *Yearbook Am. Iron Steel Inst.*, **21**, 218–93 (1931). Pfluke, F. J., *Proc. Am. Gas Assoc.*, **1931**, 936–7. Bennett, J. G., *J. Soc. Glass Tech.*, **23**, 154–70 (1939).

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[188] *Richtlinien für Vergebung und Abnahme von Schwachgaserzeugern für Kokereibetriebe*, Kokereiausschuss Ver. bergb. Int. Essen und Ver. deut. Eisenhüttenleute Dusseldorf, Essen, 1932.

[189] Anon., *Gas- u. Wasserfach*, **73**, 554–6, 577–80 (1930). Plenz, F., *Gas World*, **101**, 226 (1934).

[190] Loose, G., *Ing. & chim.*, **16**, 142–69 (1928). Bowmaker, E. J. C., and Canwood, J. D., *J. Soc. Glass Tech.*, **14**, 16–29 (1930). Francklyn, G., *Trans. Am. Inst. Mining Met. Engrs.*, **1930**, 706–13. Scales, O. L., *Blast Furnace Steel Plant*, **19**, 252–4 (1931). Gevers-Orban, R., *Rev. universelle mines*, **10**, 313–20, 347–52, 376–86 (1934).

[191] Wilson, L. M., *Fuel*, **10**, 69–71 (1931). Bateman, J., *Gas J.*, **208**, 897–9 (1934). Sweeney, J. G., *Am. Gas Assoc., Prod. & Chem. Comm. Conf.*, 1935. Qvarfort, S., *Schweiz. Ver. Gas- u Wasserfach, Monats-Bull.*, **19**, 157–62, 189 (1939); *Gas J.*, **227**, 714–9 (1939).

[192] Anon., *World Power Conf., London*, **2**, 993–1002 (1928). Schultze, K., *Glashutte*, **65**, 307–8 (1935). Möller, R., *Braunkohle*, **35**, 417–20 (1936); *Z. Ver. deut. Ind.*, **81**, 1167–71 (1937). Rammler, E., *Braunkohle*, **36**, 334–52 (1937); *Gas- u. Wasserfach*, **80**, 683–9 (1937). Wohlschläger, H., *Z. Ver. deut. Ing.*, **81**, 1299–304 (1937). Finkbeiner, H., *Arch. Wärmewirt.*, **19**, 159–62 (1938). List, H., *Z. Ver. deut. Ing.*, **82**, 455–6 (1938). Coupan, G., *Génie civil*, **113**, 421, 448 (1938). Winkelmann, H., *Feuerungstech.*, **26**, 112–3 (1938). Rammler, E., Brietling, K., and Gall, J., *ibid.*, **27**, 103–8 (1939).

TABLE V

TYPICAL OPERATING FIGURES ON LARGE MECHANICAL UP-DRAFT PRODUCERS

	I	II	III
Fuel	Coal	Coal	Coke
Size	Lumps,	Slack, 70%	97% through 1 in.
	2 to 4 in.	through ½ in.	14% through ¼ in.
Moisture, percent	1.3	9.5	10.9
Volatile matter, percent	35.0	38.0	1.9
Fixed carbon, percent	55.5	44.4	88.3
Ash, percent	8.2	8.2	9.9
Heating value (dry basis), Btu per pound	15,296	13,833	12,605
Ash fusion temperature, °F	2,780	......	2,550
Throughput dry fuel, pounds per hour	3,890	4,040	3,200
Blast	Air-steam	Air-steam	Air-steam
Air volume, cubic feet per pound dry fuel	49.0	42.8	51.6
Saturation temperature, °F	126	138	137
Steam, pounds per pound of dry fuel	0.316	0.43	0.53
Gas composition, percent			
CO_2	4.3	4.8	5.8
Illuminants	0.4	0.5	0.0
O_2	0.1	0.2	0.3
CO	26.7	25.0	26.0
CH_4	3.1	2.8	0.5
H_2	13.9	12.8	12.1
N_2	51.5	53.9	55.3
Heating value (gross), Btu per cubic foot	169.5	160.2	129.4
Temperature outlet producer, °F	1,400	1,146	1,148
Gas volume, cubic feet per pound dry fuel	68.6	63.1	74.1

TABLE VI

TYPICAL HEAT BALANCES OF A COAL PRODUCER MAKING HOT UNCLEANED GAS AND A COKE PRODUCER MAKING COLD CLEAN GAS

Input	Coal percent	Coke percent
Heating value fuel	97.6	96.2
Sensible heat, steam	2.4	3.3
air	.....	0.5
	100.0	100.0
Output		
Heating value cold gas	74.3	76.0
Sensible heat in gas	12.1	5.7
Heating value tar	5.1	.....
Output	Coal percent	Coke percent
Sensible heat in tar	0.2	.....
Heat in steam, from waste-heat boiler	.....	7.3
from jacket	.....	5.1
Heat loss, in tar, dust, etc.	2.2	.....
in cooling water	0.3	.....
in carbon in ash	0.4	1.0
in water vapor	1.9	3.8
in radiation	3.5	1.1
	100.0	100.0
Cold efficiency (based on gross heating value of cold gas)	76.1	78.9
Hot efficiency (based on useful heat in gas and tar)	93.9	86.5

TABLE VII

PERFORMANCE DATA ON OPERATION OF VEHICULAR PRODUCERS [169]

Producer, make	Wisco	Gohin-Poulenc		Koela
type	Up-draft	Cross-draft		Up-draft
Capacity, cubic meters per square meter per hour combustion area	......	....		1,540
Fuel	Low-Temperature Coke	Anthracite	Low-Temperature Coke	Low-Temperature Coke
Size	10 to 25 mm	5 to 15 mm	....	⅜ to ⅝ in.
Consumption, pounds per horse-power-hour	2.23	1	1.04	1.05
Moisture, percent	7.7	2.7	9.5	4.5
Ash, percent	8.8	6.3	....	3.7
Volatile matter, percent	13.0	6.2	....	16.6
Fixed carbon, percent	70.5	84.8	. ..	75.2
Heating value, calories per gram	7.056	7,500	....	7,346
Steam in blast	no	....	....	yes
Steam : fuel ratio	....	....	...	0.15 to 0.40
Gas				
Composition, percent				
CO_2	0.5	0.7	0.9	1.8
CO	30.6	29.3	29.7	28.6
H_2	5.3	8.5	5.6	11.6
CH_4	....	0.7	....	1.8
O_2	0.5	0.0	0.9	0.4
N_2	63.1	59.8	62.9	55.8
Heating value:				
Calories per cubic meter	1,108	1,180	....	1,250
Btu per cubic foot	116	123	....	131
Temperature at producer outlet, °C	150 to 160	400 to 500	400 to 500	180 to 230
Suction at producer outlet, millimeters water	150 to 250	....	....	....

WATER GAS

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The term water gas has been used somewhat indiscriminately to signify either the gas made by the reaction of steam on hot carbonaceous fuel or the mixture resulting from the enrichment of this gas with the hydrocarbon gases formed by the pyrolysis of oils. Further, "water gas" is an unfortunate misnomer, for it is steam and not liquid water which is used in the reaction. Since the gas formed by the reaction of steam on hot carbon is a mixture of carbon monoxide, carbon dioxide, and hydrogen, it burns with a blue flame. It has, therefore, often been called blue water gas to distinguish it from the enriched mixture to which reference has been made. The gas made by action of steam with hot carbon will be called simply blue gas in this chapter, and water gas will be reserved for the carburetted blue gas which is produced by the enrichment of blue gas with hydrocarbon gases.

HISTORY OF BLUE-GAS PROCESS

The discovery of blue gas has been attributed to Fontana, who in 1780 proposed to make it by passing steam over incandescent carbon. Although this antedates by

a dozen years the invention of the coal-gas process by Murdock, the fact that the reaction is strongly endothermic and that the gas made has no illuminating power delayed for nearly a century its serious competition with coal gas as a source of city gas supply.

The large quantity of heat absorbed in the blue-gas reactions makes it uneconomical to supply this heat by conduction to the reacting carbon. Hence the process is an intermittent one consisting of alternate "blows," or blasting periods during which the fuel in the generator is heated by blowing air through it, and "runs," or gas-making periods during which blue gas is generated by passing steam through the incandescent fuel.

In the early days, many attempts were made to enrich blue gas by light-oil vapors or by the gases resulting from the cracking of heavier oils or from the destructive distillation of rosin, cannel coal, etc. It was not, however, until 1873 that Lowe discovered how to use the producer gas made during the blows to heat checkerbrick in which enriching oil-gas is made during the runs. This invention of the carburetted water-gas process by Lowe, and an abundant supply of gas oil, a cheap byproduct in the distillation of petroleum, soon made the so-called water gas the most important

manufactured gas in the United States, and this gas still makes up nearly one-half of our manufactured gas. In addition blue gas itself has been used as a fuel in industrial plants, to mix with natural gas in supplying peak loads, and as a chemical raw material in hydrogenation and in synthetic processes. (See Chapter 39.)

THE BLUE-GAS PLANT

A sectional elevation of a blue-gas plant is given in Fig. 1. Here it will be seen that the plant consists essentially of a generator, *A*; gas offtake or "hydrogen pipe," *B*; stack, *C*; and wash box or "seal-separator," *D*. From the wash box the blue gas is led away by the hot main connection, *E*. The generator is fitted with a blast connection, *F*, and with steam connections, *G*, so that air for blasting the fire may be introduced under the grate, and steam for the gas-making runs may be introduced either at the top or bottom of the fuel bed. The blast main is provided with explosion doors, *H*, made of thin material so that they will give way first and prevent damage to the rest of the apparatus from the explosion which would occur if blue gas during the run should leak past the valve into the blast main. As a precaution against the formation of such an explosive mixture of air and hot gas, especial care must be taken to see that the blast valves remain tight. These valves may be either the butterfly or gate-valve type and are generally hydraulically operated.

The blue-gas generator consists of a steel cylinder with a refractory lining. This cylinder may be from 3½ to 15 feet in diameter and in the larger sizes has either a cone (Fig. 1) or dome (Fig. 2) top. It is fitted with a number of firebrick-lined, self-sealing doors. The coaling door, *I*, permits charging of fuel to the top of the

fire; and the clinkering doors, *J*, give access to the fire and permit removal of ashes and clinker just above the level of the grate. There is also at least one large door near the bottom which allows the removal of such ashes as may fall through the grate. This construction with the bottom of the generator on the level of the clinkering floor has the disadvantage that during the cleaning of the fire the men are forced to work over piles of steaming clinker which has been pulled out around the base of the generator and cooled with water from a hose. To avoid these conditions generators are sometimes made with hopper bottoms as illustrated in Fig. 3; the generator is supported by ironwork 8 or 10 feet above the ground floor, and an iron stage is provided for the workmen in clinkering.

The generator lining has given more trouble than any other feature in the design of the blue-gas apparatus. On account of the high and fluctuating temperatures in the fuel bed and the wear of the heavy clinkering bars during the cleaning of the fire, the generator linings wear out rapidly and have to be replaced at frequent intervals. Generator linings are usually made of fireclay blocks or brick. On account of the fluctuation of temperature in the fuel bed, silica material is not suitable for this purpose. A very high grade of fireclay must be used. This should be capable of withstanding a temperature of 3,000° F and must not flux with the ash of the fuel. The wear on the fireclay lining under usual conditions of operation is especially heavy around the lower half of the fuel bed in the region up to a distance of 3 or 4 feet above the grate. In this part the average life of the ordinary fireclay lining is about 1,000 hours of service, after which time it is necessary to shut
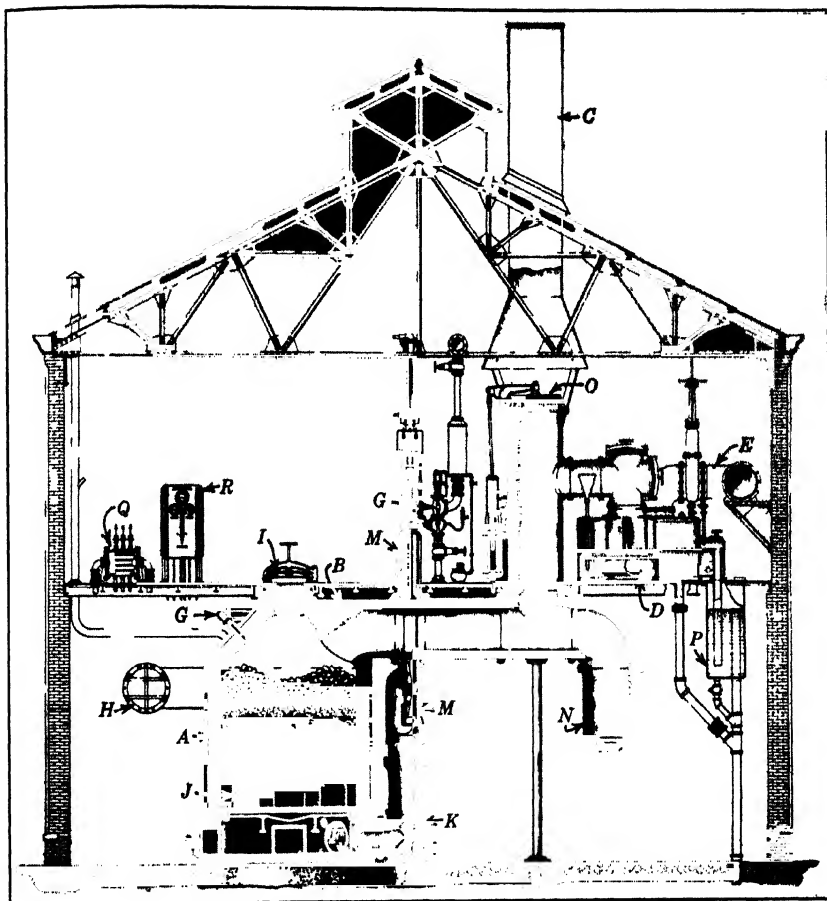
FIG. 1.   Sectional elevation of U.G.I. blue-gas apparatus.

A = generator.
B = gas offtake or hydrogen pipe.
C = stack.
D = wash box or seal separator.
E = hot main connection.
F = blast connection.
G = steam connection.
H = explosion door.
I = coaling door.

J = clinkering doors
K = bottom gas offtake.
M = hot valves.
N = dust catcher.
O = stack valve.
P = seal pot or drain tank.
Q = controls.
R = instrument board.
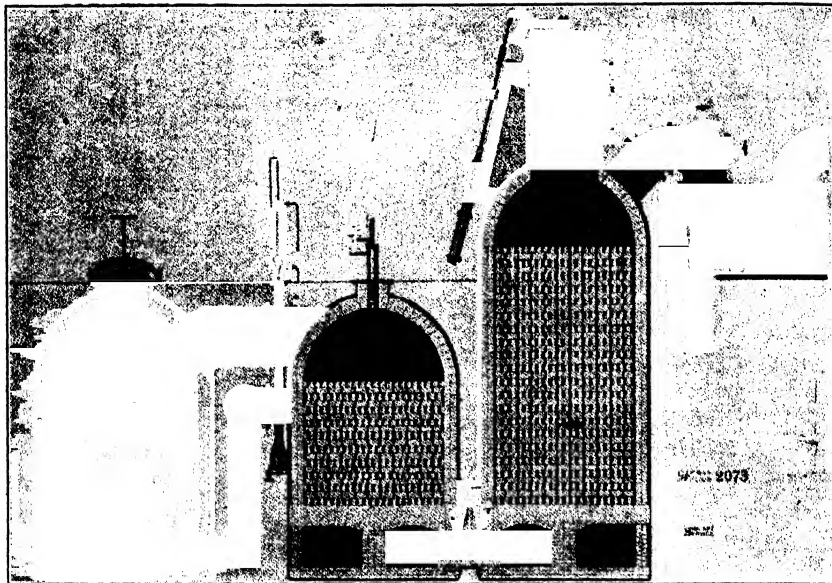
FIG. 2. Sectional view of standard three-shell water-gas set. A blue-gas generator with dome top is shown at the left of the figure.

down the generator and replace the lower part of the inner lining.

Generator linings vary in thickness according to the ideas of the builder and the size of the apparatus. In general they consist of an inner lining of firebrick which takes the wear and an outer lining which serves mainly as a heat insulator and supports the crown, especially while the inner lining is being replaced. For this purpose it is common practice in laying up the lining to use one or more courses of full-depth "headers" or deep blocks about two-thirds of the distance up from the grate so that the inner lining below this point which is subject to the most wear may be replaced without disturbing the rest of the lining. Between the outer lining and the steel shell is an insulating space of 1 or 2 inches. This allows for expansion of the lining on heating and is filled with asbestos, Silocel, Celite, or similar nonconducting materials. Typical generator lining dimensions are given in Table I. The key brick and circle brick may be replaced by straight brick cut to fit, and for the inner lining large shapes or blocks are sometimes used. The blocks reduce the number of joints which aid the clinker in clinging to the lining and are easier to lay but cost somewhat more and are more subject to spalling and cracking. For this reason, bricks larger than 9 inches in any dimension are to be regarded with suspicion whenever high temperatures or changes of temperature are concerned. If the original surface of the block or brick in the inner lining is destroyed in laying, clinker sticks badly and the block will be rapidly worn away. In laying out the dimensions, al-

TABLE I

BLUE-GAS-GENERATOR LININGS

Diameter of Generator	8 ft 6 in.	10 ft 6 in.	12 ft
Outer lining	4½-in. circle brick	4½-in. circle brick	9-in. key brick
Inner lining	9-in. key brick	9-in. key brick	9-in. key brick
Total thickness	13½ in.	13½ in.	18 in.
Insulation	1½ in.	1½ in.	2 in.
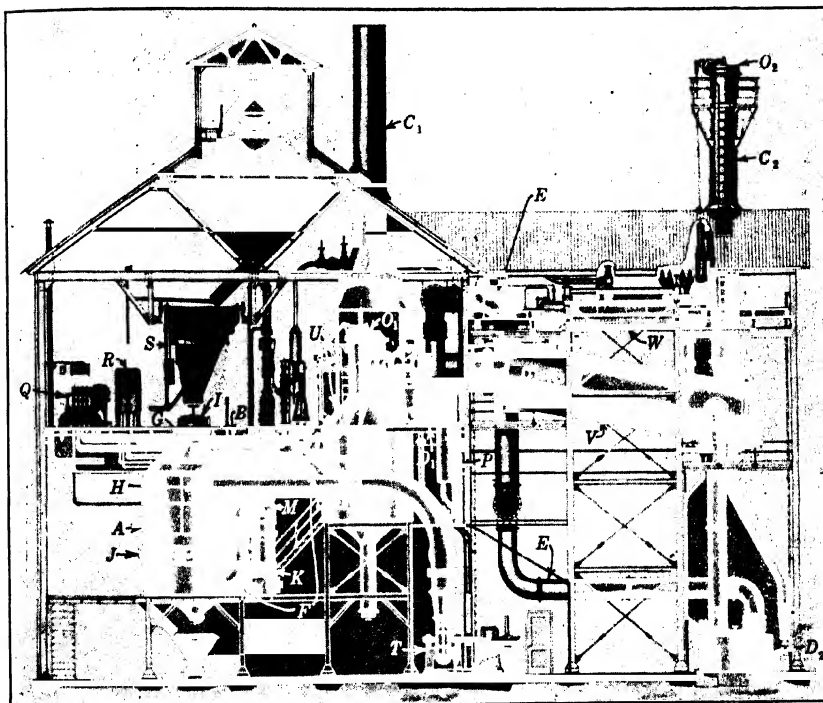
FIG. 3. Sectional elevation of U.G.I. blue-gas apparatus with igniter and horizontal waste-heat boiler.

A = generator.
B = gas offtake or hydrogen pipe.
C_1 and C_2 = stacks.
D_1 and D_2 = wash boxes.
E = hot main connection.
F = blast connection.
G = steam connection.
H = explosion door.
I = coaling door.
J = clinkering doors.
K = bottom gas offtake.

M = hot valves.
O_1 and O_2 = stack valves.
P = seal pot.
Q = controls.
R = instrument board.
S = charging larry.
T = blower.
U = igniter.
V = waste-heat boiler.
W = steam drum.

lowance is made for ⅟₁₆-inch joints which
are filled with a thin mortar of ground
firebrick and fireclay of the same compo-
sition as that of which the blocks are made.
Special refractory cements are also used
for mortar and as a coating to render the
surface of the lining smoother and less
easily subject to attack from the clinker
and wear from the clinkering tools.

Other materials used for blue-gas-gener-
ator linings include: a high-alumina clay
containing up to 80 percent alumina and
sold under the trade name Parco; high-
grade Pennsylvania flint clay, which under
the name of Plibrico is molded in place in
the generator, giving a jointless lining; sili-
con carbide, which is used either as solid
blocks or in special patented forms of lin-
ings; and water-jacketed steel, which is
used to avoid adherence of clinker in gen-
erators with mechanical grates. Some sili-
con carbide blocks or circle-brick inner
linings 4½ inches thick have been used
for 5,500 to 6,500 hours before replace-
ment was necessary. Care must be taken
to employ a grade of silicon carbide ma-
terial which will resist oxidation. Silicon
carbide is also suitable material for air-
cooled generator linings.

The Bernitz block is used in one form
of air-cooled lining in which an annular
chamber is formed between the inner and
outer linings for a distance of 5 or 6 feet
up from the grate. The chamber com-
municates with the space under the grate
and may also be connected near its top
with a bustle pipe. It communicates with
the interior of the generator by means of
two holes in the face of each 9 inch by 4
inch block in 9 or 10 rows of the lower
blocks. Thus during the blasting period
the lining is cooled by the air passing into
this chamber, and the air is distributed to
the sides of the fire through the holes in

the face of the lining. This cooling of the
lining prevents the adherence of clinker
and greatly increases the life of the lining.
When mechanical grates for automatic ash
removal are used in blue-gas generators,
just as in producer-gas apparatus, the lin-
ing around the hot zone is of water-cooled
steel. This causes the molten ash to solid-
ify before it touches the surface of the lining
and prevents it from sticking to the lining.
The water jacket of the steel lining, which
is well insulated, serves as a low-pressure
steam boiler and also preheats the feed
water of the waste-heat boiler which is
employed to recover heat from the hot
gases and blast products.

The blue-gas generator is also provided
with a bottom gas offtake, K, which con-
nects with the top gas offtake, B. By
means of a pair of connected firebrick-lined
hot valves, M, the flow of hot blue gas
is controlled so that it is taken from the
top of the fire during the up-run and from
the bottom of the fire during the down-
run. By means of a lever linked to the
hot valve stem, the flow of steam to the
fire is reversed when the position of the
hot valves is changed. To prevent ash
and fine fuel, which is carried over by the
air blast, from interfering with the proper
seating of the hot valves, the valves are
provided with an ash pocket having a self-
sealing lid at the bottom. The dust
catcher, N, also serves to collect such
material.

The gas offtake leads either to the stack,
C, or through a side connection to the
wash box, D. It consists of a large steel
pipe and is lined with firebrick. The dust
catcher or dust pot is a downward projec-
tion on the horizontal part of the offtake
pipe just beyond the point where the gas
takes an upward turn. In its place a
cyclonic dust catcher described by O'Don-

nell [1] and Battin [2] may be used. The stack valve, O, is lined with firebrick and is of the self-sealing type. It may operate on a pivot as shown in Fig. 1 or in the larger sets it may run on wheels on a track. It is open during the blow, permitting the products of combustion to pass up the stack. During the run when the stack valve is closed, the blue gas is forced to pass into the wash box, D. There it bubbles through a water seal and then passes on through the hot main connection, E. Water circulated continuously into the wash box overflows into the seal pot or drain tank, P.

In the smaller blue-gas sets the various valves may be hand operated, but, by means of extension levers and gears, the points of operation should be brought as near together as possible to avoid unnecessary loss of time by the gas maker in moving from one valve to another. In larger sets the valves are operated by electrical, hydraulic, or pneumatic power, the controls being brought together at a single control table, Q. By means of a suitable combination of cams, electrical contacts, roller link chains, or other devices, the operation of the controls may be made automatic.[3] In order that the gas maker may operate the set to the best advantage there is located near the controls an instrument board, R, on which are placed the indicating and recording mechanisms of the pyrometers, gages, and meters which show the temperatures, pressures, and quantities of materials in the various stages of the process.

Mechanical grates, as has already been indicated, are sometimes used to make ash removal automatic. They employ either a revolving cone grate [4] or an agitating and crushing beam revolving over a stationary grate.[5] Their operation will be discussed later under commercial processes.

In the operation of the blue-gas set both the blast products and the blue gas leave the generator at high temperatures. Also for economical operation the fuel bed must be deep and at a high temperature, so that the blast products contain a large percentage of carbon monoxide. Hence for efficient operation it is important that the blue-gas generator be connected to an igniter and a waste-heat boiler. Such an arrangement is shown in Fig. 3.

The igniter, or combustion chamber, U, in Fig. 3, consists of a steel cylinder with firebrick lining and checkerbrick. It is fitted with an air-blast connection so that during blow secondary air is furnished here to burn the carbon monoxide formed in blasting the generator fire and in this way enable the waste-heat boiler to recover the heat of combustion of the carbon monoxide as well as the sensible heat in the blast gases. The igniter also serves to collect dust and to mix the hot products of the combustion before they strike the tube sheet of the waste-heat boiler. In some blue-gas apparatus the igniter may take the form of the carburetter of a carburetted blue gas set.[6]

Waste-heat boilers may be either horizontal as in Fig. 3 or vertical, and of either the fire-tube or the water-tube type. Since the temperature of the gases entering the waste-heat boiler of a blue- or carburetted-blue-gas set is usually from 1,000 to

[1] O'Donnell, C. J., *Proc. Am. Gas Assoc.*, 1929, 1334–5.

[2] Battin, W. I., *Am. Gas J.*, 130, 49–50 (1929).

[3] Stevick, C. H., *Am. Gas Assoc. Monthly*, 5, 107–27 (1923). Brockhoff, H. C., *Proc. Am. Gas Assoc.*, 1930, 1684–6.

[4] O'Donnell, C. J., *Proc. Am. Gas Assoc.*, 1925, 1299–301.

[5] Ramsburg, C. J., *Proc. Intern. Conf. Bituminous Coal*, 1926, 514–39.

[6] Morris, W. R., *Proc. Tech. Sessions Am. Gas Assoc.*, 1922, 21–52.

1,600° F, under which conditions the transfer of heat is mainly by convection, in order to absorb the heat efficiently it is necessary to design the boiler so as to increase the velocity and area of contact of these medium-temperature gases. Also since these gases are usually laden with dust and sometimes tarry material special provision must be made for access to the boiler in order to clean the tubes.

OPERATION OF THE BLUE-GAS PROCESS

Although more details of operation will be given later under the discussion of commercial processes it is desirable here to outline the procedure in the production of blue gas. Assuming that we start with a new set or with one that has been out of service for major repairs to the lining, it will not be necessary to give exact operating directions for heating up the fuel bed because these are furnished by the builders of the apparatus and have been outlined elsewhere.[7] During the preliminary inspection to see that everything is in order, special consideration should be given to the necessity of properly ventilating all portions of a blue-gas apparatus before entering it. This is on account of the high percentage of carbon monoxide in blue gas and the poisonous nature of this gas. During the drying-out period, which may take 3 to 7 days, the fire is started on a 12-inch layer of clinker placed on the grate to protect it and is gradually built up until the depth of the fuel bed is 2 or 3 feet. If the set has been out of service but has not undergone repairs, the drying period is, of course, omitted and the fuel bed built up as rapidly as possible under natural draft to a depth of 2 or 3 feet. The generator is then charged with coke or anthracite to a depth of 6 or 8 feet (about 1 foot

[7] Morgan, J. J., *American Gas Practice*, J. J. Morgan, Maplewood, N. J., 1931, pp. 427–34.

below the bottom of the gas offtake) and left under natural draft for several hours until the fuel is well ignited.

Before making the first blow, the blast main is put under full working pressure, but the blast valves are left tightly closed. The generator doors are then shut tight and the ashpit purged a few seconds with steam to remove any producer gas that might remain under the grate and thus to avoid an explosion when the blast is turned on. Immediately after purging the ashpit with steam, the generator blast valve is opened slowly a few inches and left in this position until smoke and vapor from the stack valve show that the blast is passing steadily through the apparatus. The blast valve is then opened further until the pressure under the grate is about 20 inches of water. A small amount of steam may also be introduced under the grate to help protect the grate and door liners from being overheated. If the blue-gas generator is not part of a carburetted-blue-gas set or connected to an igniter and waste-heat boiler, then the blasting is continued with the products escaping up the stack until the generator fuel is hot enough for gas-making. When, however, the generator is connected with either a carburetter or igniter, before starting to make gas the rest of the apparatus must also be heated. Blasting is therefore continued in this way until the carburetter or the igniter is ready to be lighted.

When sparks and flames are seen through the sight cock of the carburetter or igniter, any steam to the ashpit is shut off and the valve admitting secondary air to the carburetter or igniter is cautiously opened 2 or 3 inches. If the gases do not ignite, steam may be admitted momentarily under the grate, but if this does not cause the gases to ignite the carburetter or igniter blast valve is immediately closed. The proced-

ure may be repeated after a short time until the gases begin to burn, but a serious explosion may occur if the secondary air is left on when the gases do not ignite. After the gases in the carburetter or igniter have lighted, the secondary air valve is opened until the flame in the apparatus is the brightest and most uniform, showing complete combustion with not too much excess air.

If the apparatus is a blue-gas set, this is a point at which the operation of the waste-heat boiler may well be started. Aside from the precautions necessary in starting any boiler plant, the waste-heat boiler is started simply by opening the second stack valve (C_2) in Fig. 3 and closing the first (C_1). Blasting may now be continued until the generator fire is hot enough for gas-making, which is usually when the top of the fuel bed as viewed through the generator sight cock becomes a dull red. During the heating of the apparatus the fire in the generator should be examined frequently through this sight cock. It sometimes happens that the top of the generator becomes too hot on account of secondary combustion with air that comes up through weak places in the fuel bed. If this occurs, to avoid overheating the generator lining, more fuel should be charged before blasting further.

Before charging fuel, any steam to the ashpit is shut off, the igniter blast and generator blast valves are closed in succession, and the charging door is opened with the usual precaution of igniting the gases with a flame on a long handle to prevent a flash. During the first few coalings, it may be necessary to close the stack valve to prevent a back-draft when the coaling door is open. If the flame after the gases are ignited at the coaling door is drawn down into the generator, it is not necessary to close the stack valve. After

coaling, if this is necessary to prevent overheating the top of the generator, the blasting is continued until the top of the fire is a dull red, when the generator is ready for the first gas-making run.

Before starting to make gas, care should be taken to see that the wash box has the proper seal, that the seal pot is full and overflowing, that all drips are clear, that the valves between the set and the relief holder, beginning with the one nearest the holder, are open, and especially that air has been purged from all apparatus into which the blue gas is to be sent. The exact procedure in purging air from gas apparatus varies with conditions. The gases most used for this purpose are products of combustion, and, where a blue-gas set is available, they are most easily obtained in its blast gases. The simplest way to purge the apparatus, especially if an igniter with waste-heat boiler, or a carburetter, is attached, would be to close the stack valve and pass the blast products, after addition of secondary air to give complete combustion, through the wash box and succeeding apparatus and to vent the expelled air at a convenient point beyond the relief holder. For maximum safety, this purging should be continued until the gas in the various pieces of apparatus shows by analysis an oxygen content of less than 5 percent by volume.[8]

The fuel in the generator having been brought to the proper temperature and everything else being in readiness, the procedure to start making gas is as follows. The igniter blast valve, the generator blast valve, and the stack valve are closed in rapid succession, and then the bottom steam, also called base steam, is turned on cautiously. On the instrument board the

8 Alrich, H. W., *Purging of Gas Holders*, Am. Gas Assoc., New York, 1933, 19 pp. Tomkins, S. S., *Proc. Am. Gas Assoc.*, 1934, 799–822.

pressures under the grate at the base of the generator and at the outlet of the wash box are noted. If the pressure at the outlet of the wash box increases, the run must be stopped by shutting off the steam and opening the stack valve. The cause of the back-pressure must then be located and removed. If there is no back-pressure, the run may be continued, but, before proceeding to make gas regularly, it is necessary to determine the length of the cycle and the proportion of the run to blow.

In fixing the cycle, especially, it is impossible to give instructions which will be at all general in their application, for conditions vary to such a large extent. A consideration of the heat effects of the reactions in the blow and in the run will suggest the principles which govern the length of the cycle and the proportions of blow and run. Since the reactions of the run absorb heat in large quantities and since those of the blow evolve heat even more rapidly, it is readily seen that a cycle of long blows and longer runs would result in wide fluctuations in the temperature of fuel bed. Such fluctuations would increase clinker troubles, and the low temperatures at the end of the long runs would markedly increase the carbon dioxide content of the blue gas. Therefore, the tendency of modern practice is toward short cycles.

On the other hand, the minimum length of cycle is fixed by the time and labor required for opening and closing valves in making the changes from run to blow, and vice versa. In a hand-operated apparatus, the labor becomes excessive if the length of the cycle is less than 5 or 6 minutes. With an automatically operated set, it is possible to shorten the cycle and thus increase the efficiency by maintaining a more even temperature in the generator and thus providing more nearly the ideal condition

of continuous gas-making. The shorter cycles tend to decrease the steam and fuel required per 1,000 cubic feet of gas but reduce the capacity when shortened below a certain limit by reason of the high proportion of time lost in the valve changes.

Since in the straight-blue-gas apparatus there is no need of maintaining definite temperatures in the other parts of the apparatus, the proportions of blow and run may be fixed with the view of obtaining the best conditions in the generator fire. Even when the apparatus is connected with a waste-heat boiler, little if any attention is paid to the temperature of ·the checker-brick in the igniter, and the blasting is carried on with the object of heating the generator fuel bed with the formation of the least possible amount of carbon monoxide. A short blow with as high a rate of blasting as is possible without blowing the fuel out of the generator is best for heating the generator bed.

In fixing the length of the run, it is to be noted that the conditions for most efficient decomposition of steam are a high temperature, a deep fuel bed, and a high rate of steaming. Since the object of the run is the production of blue gas by the decomposition of steam, it is important to know, if possible, what percentage of the steam is being decomposed. Considerable work has been done on the development of steam-decomposition meters in connection with carburetted-blue-gas sets.[9] The application of these meters in blue-gas operation is important and should present no special difficulty. It should be remembered also that there is an intimate relation between the amount of undecomposed steam and the proportion of carbon dioxide in the gas. Since carbon dioxide is the most

9 Lockwood, A. E., Huff, W. J., Logan, L., Ellis, R. L., and Carter, W. B., *Proc. Am. Gas Assoc.*, 1929, 1256–82.

objectionable as well as the most easily determinable component in blue gas, it furnishes both the reason for terminating the duration of the run and the means of telling when it is advisable to do so. Too high a rate of steaming as well as a low temperature from too long a run results in a large amount of undecomposed steam and high carbon dioxide in the blue gas. Hence, the determination of carbon dioxide in the gas is a valuable aid in establishing operating conditions.

In the actual determination of the cycle, it is necessary to use the cut-and-try method. It may be assumed that the length of the cycle should be from 4 to 6 minutes. It has been found that about 25 percent of this time should be blow. One might start with a cycle consisting of a 1.0- to 1.5-minute blow and a 3- to 4.5-minute run. Both the length of the cycle and the proportions of blow and run will vary with the fuel, the capacity desired from the set, and other conditions. Starting with the longer cycle, if the temperature at the end of the run, as shown by a low percentage of carbon dioxide in the gas, is still high, the blows might be shortened slightly or the rate of introducing steam might be increased. If the temperature at the end of the run is low as indicated by high carbon dioxide in the gas, either the length of the run or the steam rate should be decreased. If, on starting with the shorter cycle, it were found that the temperature at the end of the run is low, the remedy might be to increase the length of the blow or the rate of blasting. If the temperature were high, the run might be lengthened or the rate of steaming increased. The proper steam input to the generator to give the highest efficiency of operation with a given blast and a given fuel is found by *balancing the*

set and must be determined by experiment for each installation.

The value of the determination of carbon dioxide in fixing the conditions of the run has been discussed. The figures for oxygen and carbon monoxide in the blue gas will also be a good indication of the efficiency with which the gas-making operation is being carried on. In addition, analyses of the gases during blasting are important in establishing conditions for maximum efficiency. By means of the Orsat apparatus the percentages of carbon dioxide, oxygen, and carbon monoxide in either the blast gases or the blue gas can be found rapidly and with good accuracy. Analyses of the gases from the gas offtake of the generator and from the outlet of the igniter or of the waste-heat boiler at different stages of the blow are of much aid in finding the proper proportions of generator and secondary blast air. Conditions should be so regulated as to give as much carbon dioxide and as little carbon monoxide as possible at the first point and as much carbon dioxide and as little oxygen as possible with the absence of more than a few tenths of a percent of carbon monoxide at the second place.

The Regular Blow. The distinction between up-run and down-run has already been mentioned and will be discussed more fully later. No matter what combination is used, the last portion of the run is always up-run, so that in starting the blow the space under the grate is filled with steam and not with blue gas, which would cause an explosion when the air blast is turned on. To change from run to blow, therefore, the procedure is as follows: The steam is shut off exactly at the time fixed for the end of the run. The stack valve may then be opened and the generator blast turned on immediately thereafter. With this method of operation, the gas

which fills the top of the generator, the igniter, and the waste-heat boiler at the time the stack valve is opened is lost by being vented to the stack, where it burns. This gas may be saved by a blow purge, in which the generator blast is turned on immediately as the steam is shut off and the stack valve is not opened until 5 or 10 seconds later, during which time the gas in the set is driven through the wash box by the blast gases. With this procedure, care must be taken not to delay the opening of the stack valve too long or the quality of the blue gas will be reduced by the blast gases which are blown through the wash box. The same method is suitable whether the blue gas during the run is sent through the waste-heat boiler and the second wash box, or whether it is passed through the first wash box, and the boiler used only for the blast gases, or whether no boiler is used on the apparatus. The need for the blow purge is greater, however, when the blue gas also is being put through the boiler.

If the apparatus is connected with a waste-heat boiler the secondary air blast is not turned on until a few seconds after the opening of both the generator blast valve and the stack valve. The amount of secondary blast used will have to be determined by experience, the analysis of the gases that leave the boiler serving as the guide. These gases should contain a minimum of oxygen with practically no carbon monoxide. Since the amount of carbon monoxide in the generator blast products is less at the beginning of the blow than at the end, the secondary air valve should be opened gradually as the blow progresses. If the blue gas is not sent through the boiler, provision may be made by means of a special quick-acting valve for shutting off the boiler. All blows are then begun and ended with the first stack valve (see

Fig. 2) open, and the boiler is not fitted with a second wash box. Under these conditions one boiler is often connected to two sets which are blown alternately; to send the blast gases through the boiler, it is only necessary to open the valve connecting the boiler to the set (or the valve at the top of the boiler stack) and then to close the regular stack valve.

The Regular Run. To change to a run at the end of a blow, the secondary blast valve is closed exactly at the time fixed for the end of the blow and followed quickly by the shutting off of the generator blast. The base steam is then turned on and the stack valve closed. When the set is fitted with a waste-heat boiler and the blue gas is sent through the boiler, blast products will be passed through the wash box unless the closing of the stack valve is delayed a few seconds after the turning on of the base steam. It should then be noted from the *up-steam* meter gage whether the steam is flowing and from the pressure gages that no back-pressure is developing. Back-pressure is especially important when live steam is used, for the blue-gas apparatus is usually not built strong enough to withstand the full pressure of the boiler. Hence the shell of the apparatus is likely to rupture if for any reason, for instance if a valve falls, the gas cannot escape when the steam is turned on. Warning of this condition is usually given by the hissing of steam escaping around the coaling door, but the practice of watching the gages and inspecting them as well as the valves frequently is much better insurance against this danger.

The Down-Run and the Split-Run. During the up-run the steam which enters through the grate cools the lower part of the fuel bed both by the sensible heat necessary to raise the steam to the reaction

temperature and by the heat absorbed in the reactions of steam with the fuel. Also during the blow the cold air of the entering blast in being preheated to the reacting temperature extracts heat from the lower part of the fuel bed. The fuel in the upper part of the bed is heated by the sensible heat extracted both from hot blue gas and from the hot products of the blow. Hence a continuation of alternate blows and up-runs not only tends to deaden the bottom of the fire but also may overheat the top of the generator if the fuel is no longer cool enough to extract sufficient heat from the blast and up-run gases.

On the other hand, in the down-run, when the steam is introduced into the top of the generator and passed downward through the fire, heat is extracted from the fuel near the top and the ash and clinkers near the grate are heated by the hot blue gas. Operation with a succession of blows and down-runs would tend to give too low temperatures in the top of the generator and excessive temperatures at the bottom near the grate. Since the material near the grate is almost all ash, if it is heated to the fusing temperature it will run together and on cooling form a hard mass which interferes with the distribution of the air and steam, and it may stick to the grate. To avoid overheating the top of the generator on the one hand, and the formation of troublesome clinker on grate on the other hand, the split-run is common practice. In this the first part of the run is an up-run followed by a period of down-run and ending with another short up-run so that the space under the grate will be filled with steam and not with blue gas at the beginning of the succeeding blow.

Before describing the procedure in making a down-run, it may be well to trace clearly the path of the gases during the up-run. It has been stated that the blue-gas generator is fitted with connections so that steam may be introduced either under the grate or into the top of the generator above the fire. Also that there are both top and bottom gas offtakes and that, by means of a pair of connected hot valves, the blue gas can be caused to leave the generator by either the top or the bottom offtake. During the up-run, the hot valve in the bottom gas offtake is closed and that in the top offtake is open. Hence when steam is introduced under the grate the resulting blue gas leaves the top of the generator through the open hot valve in the top gas offtake and passes through the first wash box (see Fig. 3) or through the waste-heat boiler and the second wash box to the hot main and on to the relief holder.

In order to make a down-run, it is only necessary after the blast valves and stack valve have been closed to reverse the hot valves so that the top one is closed and the bottom one open and then to turn on the top steam. Usually a steam reversing valve is connected to the hot valve stem so that the steam is automatically reversed by the reversal of the hot valves. During the regular down-run, steam enters at the top of the generator and passes down through the fire. The blue gas leaves the ashpit through the open valve in the bottom gas offtake and passes into the hot main through the wash box, or through the waste-heat boiler and second wash box as previously described. During the down-run the ashpit is full of blue gas, and there would be an explosion in the base of the generator if the blast were turned on without first purging the ashpit for a few seconds with bottom steam. It is, therefore, necessary when making a down-run to reverse to an up-run for at least a few seconds before changing to the blow. Also it is readily seen that, if the stem of one of the hot valves should break so that both

remained closed when the steam was
turned on, the pressure in the generator
might build up to a point where there
would be danger of a rupture of the gen-
erator shell.

Charging Fuel to the Generator. Fuel
should be charged to the generator at regu-
lar intervals in order to maintain a uni-
form depth of fuel bed. With hand charg-
ing, the fuel is introduced into the gener-
ator at the beginning of a blow. After
changing from run to blow, the blast is
left on for a few seconds to purge the blue
gas from the apparatus, the blast valves
are then closed, and the coaling door opened
cautiously an inch or two. If the gases
in the generator do not ignite, they are
lighted with a torch and then the coaling
door is opened wide.

The frequency of charging depends upon
the charging facilities, the kind of fuel, and
the length of cycles. In deciding upon
the frequency of charging, it should be
borne in mind that the more frequently
the fuel is charged the more uniform will
be the fire. On the other hand, too fre-
quent charging causes excessive loss of
time and reduces the capacity of the set.
It is often held that not more than 4 to 6
minutes per hour should be used in
charging.

The proper depth of the fuel bed will
vary according to local conditions, fuel,
blast pressure, etc. It is usually 6 to 9
feet, but the top of the fire should not be
kept high enough so that fuel is blown
over by the blast.

The methods of hand charging also vary.
The usual methods are dumping by hand
barrows in smaller sets, and chuting from
suspended lorries in larger sets. Provision
should always be made for weighing the
fuel charged.

The surface of the fuel should be kept
level or at least no higher at the center

than around the sides. For spreading the
fuel in charging various devices are em-
ployed, including scoops specially designed
for the purpose, and a simple sheet-iron
cone suspended in the coaling hole from a
T-rod. The fuel should be delivered along
the sides where the fine material remains
while the lumps roll into the center. This
arrangement opposes the tendency of the
fire to become open along the walls and
dense in the center.

To avoid loss of time in charging and
to aid in maintaining uniform conditions in
the fire automatic chargers have been de-
veloped, one of which [10] is illustrated in
Fig. 4. The charger in Fig. 4 consists
generally of a cast-iron body with an
upper sliding gate for admitting fuel to
the charger and a lower bell gate for drop-
ping the fuel into the generator. Both
gates are operated by hydraulic cylinders
which in turn are operated from the master
valve and automatic control machine. The
volume of fuel per charge may be adjusted
by means of a movable cylinder within the
charger body. Automatic chargers are of
special value when bituminous coal is the
fuel because they keep the evolution of
coal gas from the green charge uniform
and if the fuel is introduced during the
down-run part of cycle the tar vapors
evolved may be decomposed by the pas-
sage through the generator fuel bed. They
tend to make the condition of the fuel bed
more uniform, and they may increase the
capacity about 15 percent, of which 6 to 8
percent is due to the time ordinarily lost
in hand charging and the remainder to the
more effective gas-making conditions of
the fire.[11]

10 Slowe, T. W., *Proc. Am. Gas Assoc.*, **1924,**
861–2, **1925,** 1307–10. O'Donnell, C. J., *ibid.,*
1929, 1335–6.
11 Sperr, F. W., Jr., *Chem. & Met. Eng.*, **31,**
853 (1924).

When charging is not automatic, special care should be taken to see that time is not wasted in coaling. As soon as charging is completed, the charging door seat is swept clean and the door closed. The generator blast valve is then cautiously opened and the blow continued. The first blow after
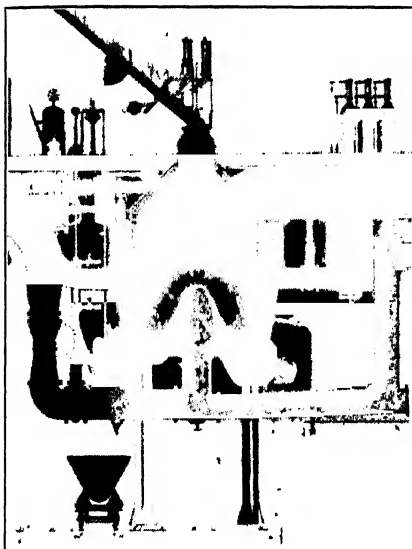
FIG. 4. Sectional view of U G I. mechanical blue-gas generator with automatic charger.

coaling is usually somewhat longer than the regular period. If for any reason the generator has been open for a time in charging, the ashpit should be purged a few seconds with steam before the generator blast valve is opened.

Clinker Formation. In discussing the formation of clinker in the blue-gas generator, it must be noted that conditions are quite different from those in the gas producer where the temperature is fairly uniform and where clinker formation can be largely prevented by use of steam. The blasting of the blue-gas generator is done

without steam, and at the end of the blow the temperature is considerably higher than is common in good producer practice. It may reach 2,800 or 3,000° F, which will cause some fusion in the ash of practically any coal or coke. The question in the blue-gas generator is not whether there will be clinker, but whether it will be formed so as to give excessive trouble in its removal. It is the nature and place of formation of the clinker that are important. In this connection the fusing point of the ash of the generator fuel also becomes important. The analysis of the ash in the fuel is probably of little consequence except in its influence on the ash-fusing point.

Warnick, who has made a study of causes of clinker formation, found that the analysis of ash for the best results should show about equal proportions of silica and alumina, a minimum amount of calcium oxide, and the lowest possible percentages of iron oxide, magnesia, and alkalies.[12] This analysis points to a rather high-fusing ash although the fusion point can be only roughly judged from the analysis (see Chapter 15). However, it is not the fuel having the highest ash-fusion point that always gives the best results. According to Warnick, "Experience has shown that clinker troubles are minimum when the fusing temperature of the ash is between 2,300° F and 2,500° F." This is a medium ash-fusing point.

In explaining the influence of ash-fusing point on the place where the clinker will be formed, it must be remembered that clinker is not formed by the fusion of the ash but by the solidification of the fused ash. Also on account of the cooling effect of the steam of the runs and of the cold blast during the blows on the bottom of

12 Warnick, J. H., *Proc. Am. Gas Assoc.*, **1924,** 816–9.

the fuel bed, the zone of maximum temperature is up some distance from the bottom of the fire. Keeping these points in mind it will be seen that, with an ash of high fusing point, the solidification of the fused material takes place just below the zone of maximum temperature. This causes deposition of clinker high up on the generator lining and inclusion of much carbon in the solidified mass. On the other hand, with fuel of low-fusing ash, the mass remains liquid down to the bottom of the fire and gives trouble by solidifying and sticking on the grate in a dense form. When the ash has an intermediate fusing point, it remains liquid part way down from the hottest zone. This allows the remaining fuel to be burned out and the ash solidifies gradually as the fuel is consumed, forming a more porous and easily crushed clinker and sticking neither to the grate nor high up on the lining.

This explanation seems to account for the fact which Warnick has noted that fuel with ash of medium fusing point gives less clinker trouble. He also called attention to the facts that short cycles which tend towards uniform temperatures in the fire decrease clinker troubles, and that there is a relationship between the fusing point of the ash and the amount of air that can be blasted through the fire during the blow. According to him, if the fusing point of the ash is as low as 2,200° F, not more than 350 to 400 cubic feet of air should be used per square foot of grate per blow. If the fusing point of the ash approaches 2,600° F, 500 to 550 cubic feet of air may be used per square foot per blow.

A good understanding of the manner of clinker formation as given above is helpful not only in the choice of fuels according to the fusing point of the ash but also in showing the reasons for using one method of cleaning the fire when the fuel has a low-fusing ash and an entirely different method for fuels with ash of high fusing point.

Cleaning the Fire. It has been noted above that in the operation of the blue-gas generator it is not a question of whether clinker will be formed but whether or not this clinker will be formed in such a manner as to give excessive trouble in its removal. Therefore, unless an automatic grate is used, it is necessary to clean the fire at intervals, and the frequency of the cleaning will depend upon many conditions. The fire should be cleaned whenever there is a sufficient accumulation of clinker and ash to interfere seriously with the passage of the air and steam through the fuel bed. Pressure gages which show the difference in pressure below and above the fuel bed both during the blow and during the run are helpful in indicating the condition of the fire.

There are two general methods of cleaning the fire; the one to be chosen depends, as previously inferred, upon the fusing point of the ash of the fuel. Conversely, the choice of fuel may to some extent be made according to the fusing point of its ash and the method of cleaning the fire which it is desired to employ. The two methods are the deep fire or hold-up bar method, which is used with fuels of low fusing point, and the low fire or barring-down method employed with fuel whose ash has a high or medium fusing point. The choice of the method and the procedure depends upon the location of the clinker formed, as has been explained.

With generator fuel having a low fusing ash (say below 2,300° F), there will be little or no side-wall clinker even with a solid lining of fireclay. The reason is that the walls are hot enough so that the ash does not solidify and form clinker high up on the side walls. Instead it remains liq-

uid until it runs down near the grate. Hence with a low-fusing ash the clinker collects in the bottom of the fire near the grate. The fire may then be cleaned when the generator is full of fuel, even right after coaling.

To clean such a fire by the hold-up bar method, the apparatus is blasted long enough after a run to purge out the gas and then the blast is shut off as in coaling. The ashpit and clinkering doors are cautiously opened, care being taken to avoid chance of injury from a flash. Heavy clinkering bars (1.5 to 2.0 inch square iron) are then driven in, supported at the top of the clinkering doors by cross bars which rest on lugs on the door jam. These bars hold up the fire while the clinker below them is broken up with chisel bars and raked out. After the grate and ashpit have been cleaned, the hold-up bars are removed, the clinker doors are closed, and the apparatus is then ready for the blow to proceed. This method of cleaning has the advantage that after the cleaning the generator is still partly full of fuel. It has the disadvantage that the clinker which often collects in a large dense mass on the grate is difficult to break up and remove.

With fuels whose ash has a medium or high fusing point (say above 2,300° F), the solidifying point of the fused ash is above the temperature of the generator walls, and hence the fused ash which finds its way to the walls is solidified and clings to them fairly high up from the grate. There it cannot be removed by the hold-up bar method; the barring-down method must be used, and before cleaning it is necessary to allow the fire in the generator to burn down low. The clinkering and ash doors are then opened and all the clinker possible is broken up and raked out, leaving only a small amount of live fuel on the grate. The clinkering and ash doors are then closed and the coaling door opened. The side-wall clinker is now broken off with heavy chisel bars worked through the coaling door. It is often necessary to use a sledge on the chisel bar to cut away the wall clinker. Clinkering machines, usually consisting of an arrangement for raising a heavy bar which is then dropped on the clinker, have been devised for lightening the labor in this operation, but their use is not common. Generally the work is done by two strong men working together on each bar and being relieved every few minutes by two other men. A large share of the wear on the generator lining is caused by the clinkering tools in this method of cleaning the fire.

The side-wall clinker thus removed is left on the grate until the next cleaning period. It, together with the small amount of live fuel left on the grate and the heat of the generator walls, serves to kindle the fresh fuel which is charged into the generator after cleaning is completed. This method of cleaning has the disadvantages of excessive wear on the generator lining, and loss of capacity caused by inefficient decomposition of steam in the shallow fire previous to the cleaning period and by the extra time consumed in the long blows which are necessary to bring the fire into good condition after the generator has been filled completely with cold fuel. The disadvantages of manual cleaning of the fire may be overcome by mechanical grates, the use of which is increasing.

Shutting down a Blue-Gas Apparatus. One of the great advantages of the blue-gas apparatus is its adaptability for standby service. It can be brought into operation in a few hours, even when cold, and it can be shut down on a few minutes' notice. When the apparatus is to be shut down, the last run should be an up-run. To close down the apparatus all steam and

blast valves are closed and the stack valve is left open. The blower and any unnecessary pumps are shut down, the gas-outlet valve on the wash box is closed, and the wash-box water-supply valve is throttled down so that only a small stream is flowing. If the apparatus is not to be idle more than 16 to 18 hours, the fire may usually be kept without any air passing through it. Sometimes, on account of the small size or the nature of the fuel, it may be necessary to furnish some natural draft by opening the ashpit door and regulating the draft by the amount of the opening.

General Operating Precautions. Special operating instructions furnished by the builders of the blue-gas apparatus give exact directions for the operation and care of the set. These instructions should be obtained and carefully studied before any attempt is made to operate a blue-gas set.

In the general operation it should never be forgotten:

1. That in the blue-gas apparatus one is handling enormous volumes of air under pressure and of hot combustible gas and that a disastrous explosion may result from any mixture of large quantities of the two. Modern apparatus is provided with an interlocking system so that it is nearly impossible to open a valve at the wrong time, but there are still plenty of sources of danger so that constant vigilance is necessary. Particularly hot valves, blast valves, and boiler valves should be inspected regularly and often to see that they are seating properly and are tight and in good working condition. The danger from a broken hot valve stem has already been mentioned. The accumulation of a mixture of blue gas and air in the blast main or in the waste-heat boiler caused by a leaky valve can easily lead to a violent explosion.

2. That blue gas contains a large percentage of the deadly poison, carbon monoxide, which is all the more dangerous since it is odorless and invisible. No one should be allowed to enter any part of a blue-gas apparatus without the most careful precautions to insure that the apparatus has been properly vented and is free from any remaining traces of gas. In this connection it is said that the only safe way to vent a wash box is to flood it with water.

3. That there is always danger of a flash when one of the doors of the apparatus is opened to the air. Hence, as has been directed in the previous discussion, the greatest care is necessary to see that no one is where he can be reached by any flash when a door is opened. Also, since blue gas is 50 percent hydrogen which diffuses and forms an explosive mixture with air the most rapidly of any gas, it is especially necessary to avoid touching off such a mixture with an open light or spark when any part of the apparatus which contains blue gas is open.

4. That the rules of good housekeeping apply to good operation. Everything in connection with the apparatus and accessories should be kept clean and in the best working order at all times.

MECHANICAL GRATES

The elimination of the dirty, arduous, and hazardous work involved in the normal cleaning of the fire in the blue-gas generator was one of the dreams of gas engineers for a long time. Since 1925, however, real progress has been made. According to Wolfe,[13] the first mechanical grate applied to a water-gas generator in the United States was in 1924; in 1925, a second installation of a different type of grate

[13] Wolfe, J. H., *Am. Gas J.*, **133**, No. 4, 45–8 (1930).

was made, and during the next two years the operation of these grates was carefully studied. Real growth began in 1927 when there were 7 generators with mechanical grates in operation. In 1928, this number grew to 19, during 1929 it increased to 35, and by the end of 1930 there were 50 generators with mechanical grates in operation or under construction. Since then the growth though less rapid has been substantial. In 1937,[14] there were 36 A.B.C. self-clinkering grates in service in industrial and utility plants, and in 1938[15] a total of 48 U.G.I. mechanical generators had been installed. In addition there are smaller numbers of other types.[16] ·

The first installation of the U.G.I. mechanical generator was made in Philadelphia in 1924.[4] In its latest form, this apparatus as shown in Fig. 4 has a revolving cone-shaped grate somewhat like that of a U.G.I. gas producer. Instead of the grate being water sealed as in the gas producer, the joint between the revolving grate and the stationary shell of the generator is made gas tight by a special gasket system. The ash and crushed clinker are discharged continuously by the revolving grate into a gas-tight receiver from which they are emptied at intervals. The U.G.I. mechanical generator also resembles the gas producer in that it has no refractory lining except at the top of the fuel bed. Perhaps the most difficult problem in the development of the mechanical grate for blue-gas generators was that of avoiding, or removing, side-wall clinkers. In the U.G.I. mechanical generator, as in the gas producer, this is accomplished by means of a water-jacketed steel lining which forms an annular low-pressure boiler surrounding

the clinker zone. This cools the lower portion of the fuel bed near the walls so that the molten ash is solidified before it reaches the lining and therefore does not adhere. The heat which is taken from the fuel bed in this way is recovered in the form of low-pressure steam generated by the lining jacket and used in the generator for gasmaking. In the later form of generator, the deck ash pan has been made renewable and the drive mechanism has been simplified.[15] The earliest installation of the A.B.C. automatic grate, made in Chicago in 1925,[5] consisted essentially of a stationary horizontal grate over which revolved a hollow, water-cooled cast-steel beam. The revolving beam had its forward, or working, face so shaped that it pushed upward part of the material at the bottom of the fuel bed and at the same time forced outward and crushed against the side walls any large masses of clinker which may have come down to the grate. The ash and crushed clinker fell through tapered slots in the grate. These tapered slots were larger on the underside and also at the end away from the moving face of the beam. The movement of the beam therefore aided the passage of the clinker and ash and also tended to clean the slots. The speed of rotation of the breaker beam was from 0.5 to 3 revolutions per hour and was designed to produce a wavelike motion in the fuel bed starting at the grate in waves about 15 inches high and extending upward about 5 feet. The slow wavelike motion, it was thought, tends to keep the fire uniform and to prevent the formation of blow holes and of large lumps of clinker. The outward movement caused by the revolving breaker beams opens up the center of the fire and packs the material against the walls so as to give it more uniform passage of air and steam through the fire.

14 Merritt, M. H., *Proc. Am. Gas Assoc.*, 1937, 687.

15 Schlegel, C. A., *ibid.*, 1938, 684.

16 Oliveros, R. P., *ibid.*, 1932, 928–41, 1936, 832.

In the original design of the A.B.C. grate a water-cooled crushing ring extended up about 18 inches from the top of the grate. In later designs this was replaced by the ordinary refractory lining which was brought down to the grate [17] or by a water-jacketed steel lining which served as an annular steam boiler and was heavily insulated.[18] In later designs, the water cooled S-shaped beam revolving over a stationary grate has been retained,[19] as well as the heavy steel cone for introduction of steam and air and the single hydraulically operated ash door and ash plows. The driving mechanism of the revolving beam consisted of two hydraulic cylinders which operated pusher rods that engaged the teeth on the ratchet ring carrying the breaker beam. Later a simplified motor-driven, direct bevel gear drive was used.[14]

Other developments in mechanical grates for blue-gas generators include: a steam-jacketed self-clinkering automatic grate generator based on the Koller patents and announced by the Semet-Solvay Engineering Corporation; [16] the U.G.I. Model C mechanical grate for use on existing flat-bottom generators; [20] the licensing for the United States by the Semet-Solvay Engineering Corporation of the Power-Gas Corporation's mechanical generator with the Lymn-Rambush grate; [16] and the announcement by the Koppers Company, Western Gas Division, of the Hayes mechanical grate for smaller generators using bituminous coal as fuel.[14]

Advantages of mechanical grates which have been proved include:

1. The labor of hand clinkering is entirely eliminated. U.G.I. mechanical generators with water-cooled walls have operated for as long as 10 months without interruptions. Others have been reported [21] to operate continuously for 50 to 199 days or continuously between checkering periods of the carburetter in a water-gas set. The removal of the ash from the hoppers requires the part-time service of 1 man. The labor of the clinkering squad of 5 or 6 men is saved.

2. A marked increase in capacity results partly from time gained since the set does not require shutting down for clinkering and partly from gain in efficiency caused by the more uniformly active fuel bed. The total gain may be as much as 20 percent.

3. There is a decided decrease in the percentage of fuel removed with the ash in mechanical operation as compared with hand clinkering. This saving is partly reduced by the heat carried away in the cooling water of the revolving beam or in the steam made in the annular boiler jacket. When the water-jacketed lining is used, the outside is heavily insulated so that part of the steam made results from heat that otherwise would be lost by radiation. Tests with the U.G.I. grate [22] showed that the combustible in the ash from the mechanical grate was less than 5 percent as compared with about 25 percent for a standard generator. Figures given for the A.B.C. grate [5] indicate that the carbon in the material from the automatic grate was 15 percent less than for hand operation. Savings of 1 to 1.7 pound of fuel per 1,000 cubic feet of gas have been reported.[23]

4. There is a saving in generator linings with mechanical grates. In the water-jacketed generator, lining repairs are prac-

17 Young, H. B., *ibid.*, **1930,** 1600–1.

18 Brockhoff, H. C., *Gas Age-Record,* **67,** 948–52 (1931).

19 Brockhoff, H. C., *Proc. Am. Gas Assoc.,* **1931,** 1202–4.

20 Schlegel, C. A., *ibid.*, **1933,** 820, **1936,** 844.

21 Brockhoff, H. C., *ibid.*, **1931.** 1173–4.

22 O'Donnell, C. J., *ibid.*, **1928,** 1370–1.

23 Schlegel, C. A., *ibid.*, **1931,** 1172–3.

tically eliminated. With other types the wear on the lining caused by barring down side-wall clinker is greatly decreased or entirely eliminated.

Against these advantages must be put the increased cost of installation and the maintenance of the mechanism. The increased installation cost is usually far outweighed by the increased capacity which with the mechanical grate results in a decrease of the total carrying charges per unit of capacity. Experience has shown that the maintenance on the mechanical grate is not excessive, and reports on some installations show that the maintenance costs on mechanical generators are definitely lower than those incurred with hand operation.[24] Maintenance costs on mechanical generators have been given from 0.06 to 0.21 cent per 1,000 cubic feet of gas, and a net saving of $7,000 per year has been reported.[23] Results secured with an installation of nine U.G.I. mechanical generators in an industrial plant where the gas was measured and the fuel weighed showed:

Make per day per set	5,760,000 cu ft
Fuel used per 1,000 cu ft	25.35 lb
Btu per cubic foot of gas	244

THEORY OF THE WATER-GAS PROCESS

REACTIONS DURING THE BLOW

The main object of the blow in the straight-blue-gas process is to store up in the fuel bed of the generator heat which may be used for the decomposition of steam during the gas-making period. In the carburetted-water-gas process, the blow also serves to make producer gas to heat the part of the apparatus which is used to make oil gas from the carburetting materials. Even in the straight blue gas apparatus it is necessary to operate with a thick fuel bed so that the product leaving the top of the fuel bed is a lean producer gas fairly high in carbon monoxide.

The reactions of the blow, therefore, are those of the gas producer when operated with dry air, which are given here together with the amounts of heat evolved or absorbed in the reaction of pound-molar quantities (12.01 pounds of carbon and 32.00 pounds of oxygen) at 1,832° F (1,000° C). The values for the heat involved in these reactions are based upon $14,434 \pm 10$ Btu per pound of carbon in anthracite coke burned to carbon dioxide at 77° F; [25] $4,345.5 \pm 1.8$ Btu per pound of carbon monoxide burned to carbon dioxide at 77° F; [26] and the heat capacity of the gases as given by Eastman.[27] The equations which give the heat involved in Btu per pound mole at any temperature, $t°$ Fahrenheit, are:

(1) $\quad C + O_2 = CO_2 + 173,325 + 0.32t$
$$+ 0.0_4331t^2 - 0.0_7154t^3$$

(2) $\quad C + CO_2 = 2CO - 69,825 - 2.46t$
$$+ 0.0_2219t^2 - 0.0_6227t^3$$

(3) $\quad C + \frac{1}{2}O_2 = CO + 51,750 - 1.07t$
$$+ 0.0_2111t^2 - 0.0_6121t^3$$

(4) $\quad CO + \frac{1}{2}O_2 = CO_2 + 121,575$
$$+ 1.386t - 0.0_2107t^2 + 0.0_6105t^3$$

From these equations, it may be calculated that

(1a) $\quad C + O_2 = CO_2 + 173,930$ Btu
$$\text{at } 1,832° \text{ F}$$

(2a) $\quad C + CO_2 = 2CO - 68,400$ Btu
$$\text{at } 1,832° \text{ F}$$

(3a) $\quad 2C + O_2 = 2CO + 105,530$ Btu
$$\text{at } 1,832° \text{ F}$$

[24] Schlegel, C. A., *ibid.*, **1931**, 1198–1201.

[25] Dewey, P. H., and Harper, D. R., *J. Research Natl. Bur. Standards*, **21**, 457–74 (1938).
[26] Rossini, F. D., *ibid.*, **6**, 37–49 (1931).
[27] Eastman, E. D., *U. S. Bur. Mines, Tech. Paper* 445 (1929), pp. 1–27.

(4a) $2CO + O_2 = 2CO_2 + 242,330$ Btu
                                at $1,832°$ F
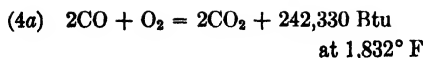
It is not to be inferred, however, that the reactions in the fuel bed take place at this particular temperature, but they do occur at high temperatures, and the quantities of heat involved in the reactions at the temperatures at which the reactions do take place are certainly much nearer to the amounts given for $1,832°$ F than they are to the amounts for the lower temperatures ($60°$ F, or $0°$ C, or $25°$ C) which are often used as standards in thermodynamical discussions. Since in these reactions air and not pure oxygen is involved, the quantities of nitrogen accompanying the oxygen in the air may be included in the reactions which then serve as the basis for discussions of the volumes of gas involved.

(1b) $C + O_2 + 3.76N_2 = CO_2 + 3.76N_2$

(2b) $C + CO_2 + 3.76N_2 = 2CO + 3.76N_2$

(3b) $2C + O_2 + 3.76N_2 = 2CO + 3.76N_2$

(4b) $2CO + 3.76N_2 + O_2 + 3.76N_2$
                        $= 2CO_2 + 7.52N_2$
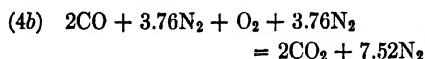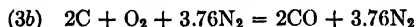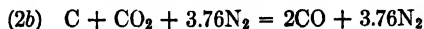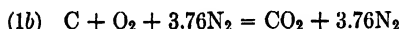
These reactions are also discussed in detail in the section on the gas producer (see page 1587). In the blue-gas generator during the blow, the oxygen of the air which enters through the grate is changed to carbon dioxide according to reactions 1 at an extremely rapid rate. The reaction is completed so that all the oxygen is used up a few inches above the ash line. These 5 or 6 inches at the bottom of the active fuel form the oxidation zone. Increasing the rate of air blasting does not materially increase the thickness of this oxidation zone but does increase in direct proportion the weight of fuel consumed per square foot of grate area. Consequently, increase in the rate of blowing raises the temperature of the oxidation zone and of the fuel above this zone.

As soon as most of the oxygen in the blast is used up, the carbon dioxide formed begins to react with the hot carbon according to reaction 2. This reaction is much slower than reaction 1 so that it requires a time of contact of a few seconds to convert most of the carbon dioxide to carbon monoxide. The reduction zone in which carbon dioxide is reduced to carbon monoxide may, therefore, be 2 or 3 feet in thickness. It extends from the top of the oxidation zone to the place where the temperature is low enough so that the rate of reaction 2 becomes negligible. Since reaction 2 absorbs heat, not only its rate but also the proportion of carbon dioxide changed to carbon monoxide at equilibrium is increased by a rise in temperature.

Reaction 3 is the sum of reactions 1 and 2 and expresses the overall conversion of carbon and oxygen to carbon monoxide.

Reaction 4 takes place in the blue-gas generator only if oxygen reaches the top of the fuel bed on account of blow holes in the fuel or cracks in the refractory lining, or is purposely introduced into the generator over the fire. It is the reaction for the combustion of the carbon monoxide in the blast products by secondary air which is regularly introduced into the igniter of the blue-gas set or into the carburetter of the water-gas apparatus.

Above the reduction zone is a zone of preheating fuel, if the fuel is coke; if it is bituminous coal, the preheating fuel zone will be merged with a distillation zone in which the volatile matter in the coal is expelled by heat brought to the coal by the hot blast products. It must not be assumed, however, that these zones are horizontal layers in the fuel bed of the generator. Terres [28] has shown that in the

28 Terres, E., *Gas World*, **90**, 438–9 (1929).

gas producer there is an oval central core in which the best gas, highest in carbon monoxide and lowest in carbon dioxide, is produced. On account of the cooling effect of the walls and the increase in the rate of gas flow around the periphery of the fuel bed, the gas decreases in carbon monoxide and increases in carbon dioxide as the distance from the walls decreases. These zones are curved up around the walls, and the boundaries between them are not definite, sharply defined surfaces.

As has been indicated, the primary object of the blow in a blue-gas generator is to bring the fuel up to the proper temperature for the decomposition of steam during the succeeding run. To be efficient this must be done with the combustion of the least possible amount of fuel. In addition to the loss of heat by radiation, which can be largely overcome by the proper design of the generator, the main losses of heat are through sensible heat in the blast products and through incomplete combustion of carbon to carbon monoxide according to reaction 3. Since the amount of oxygen entering into reaction 3 is the same as that in reaction 1, it is evident that to obtain a given quantity of heat in the fuel bed more air as well as more carbon will be required when the carbon goes to form carbon monoxide than when it goes to form carbon dioxide. Hence the loss of sensible heat is also greater when the blow gases contain a larger percentage of carbon monoxide.

In order to heat the blue-gas-generator fuel more economically, it is desirable, therefore, to have a rather shallow fuel bed and to use a high blast pressure for both these conditions; reducing the time of contact thereby favors the formation of carbon dioxide rather than carbon monoxide in the blasting. The use of a high blast pressure up to about 40 inches of

water pressure is advantageous and a characteristic of modern practice in blue-gas operation. Difficulties with high-pressure, high-speed blowing apparatus, and the amount of fine fuel carried along by the blow gases at high velocities, limit the blast pressure which it is practical to employ. On the other hand a shallow fuel bed, which is desirable during the blow, does not give the conditions required for the decomposition of steam during the run so that a compromise is necessary and considerable carbon monoxide is always formed during the blow. By connecting the generator with a combustion chamber and waste-heat boiler not only the potential heat of the carbon monoxide but also a large part of the sensible heat of the blast gases can be recovered. With these accessories it is customary to regulate the depth of the fuel bed, in the straight-blue-gas process as well as in the water-gas set, by the depth which is desirable for efficient decomposition of steam during the run.

The length of the blasting period together with the volume of air passing per unit time determines the temperature which will be obtained in the fuel bed. Higher blast pressures give more carbon dioxide in the blast products and allow shorter blowing periods. This promotes fuel economy in the heating of the generator itself. As will be shown in the consideration of the reactions during the run, the most desirable temperature for the fuel bed in the blue-gas generator is as high as clinkering conditions will permit. This is a condition more favorable for carbon monoxide formation and is a reason for the use of waste-heat boilers in connection with the blue-gas apparatus.

REACTIONS DURING THE RUN

In spite of considerable difference of opinion as to the exact sequence of the

reactions by which blue gas is formed from carbon and steam, writers on the subject are fairly well agreed that these reactions are represented by some combination of the following:

(5) $C + H_2O = CO + H_2 - 53{,}850$ Btu
$$\text{at } 1{,}832° \text{ F}$$

(6) $C + 2H_2O = CO_2 + 2H_2 - 39{,}350$ Btu
$$\text{at } 1{,}832° \text{ F}$$

(7) $CO + H_2O = CO_2 + H_2 + 14{,}500$ Btu
$$\text{at } 1{,}832° \text{ F}$$

(8) $C + CO_2 = 2CO - 68{,}400$ Btu
$$\text{at } 1{,}832° \text{ F}$$
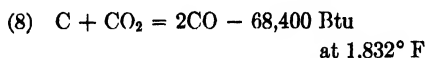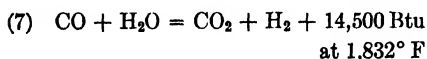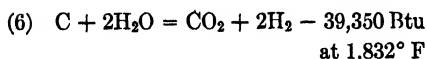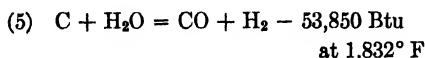
The values for the heat involved in these reactions are based upon the values for carbon and carbon monoxide and the heat capacities given previously and upon the net heating value of hydrogen to water vapor of 51,623 Btu per pound at 60° F.[29] The value of 2.016 pounds of hydrogen per mole is used. The equations which give the heat involved in Btu per pound mole at any temperature, $t°$ Fahrenheit, are:

(5a) $C + H_2O = CO + H_2 - 52{,}200$
$$- 3.148t + 0.02108t^2 + 0.078t^3$$

(6a) $C + 2H_2O = CO_2 + 2H_2 - 34{,}575$
$$- 3.836t - 0.04343t^2 + 0.06385t^3$$

(7a) $CO + H_2O = CO_2 + H_2 + 17{,}625$
$$- 0.688t - 0.02111t^2 + 0.063t^3$$

(9) $H_2 + \frac{1}{2}O_2 = (H_2O)_g + 103{,}950$
$$+ 2.078t + 0.04337t^2 - 0.062t^3$$
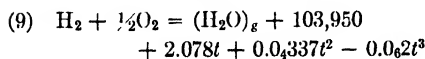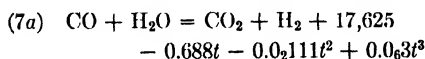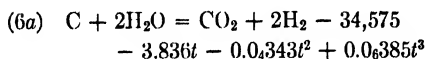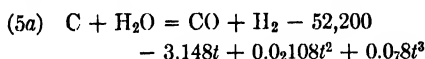
To emphasize the facts that these reactions take place only at high temperatures and that it is steam not liquid water which reacts, the quantities of heat involved in the reactions at 1,832° F (1,000° C) have been used in the equations. It is not to be inferred that these reactions take place only at the temperature of 1,832° F, but the amounts of heat involved at the high temperatures at which the reactions do take place are much nearer to those given for 1,832° F than they are to those which would be given if the reactions were written for the conventional temperature of 60° F or of 0° C.

As to the sequence of the reactions in the formation of blue gas it will be seen that equations 5 and 6, if they are assumed to take place simultaneously, account for the facts that the resulting blue gas is a mixture of carbon monoxide, carbon dioxide, and hydrogen, and that a large amount of heat is absorbed in the process. It will also be seen that, in accord with Le Châtelier's law, reaction 5 which absorbs more heat than 6 should be favored by higher temperatures, a prediction which is in agreement with the observation that the percentage of carbon monoxide obtained in practice is greater at higher temperatures. These explanations account satisfactorily in a qualitative way for the formation of blue gas. It is to be noted also that reaction 7, which is reversible, merely expresses an adjustment towards equilibrium of undecomposed steam and the products of reactions 5 and 6; further, that equation 8 represents the reaction of more carbon with carbon dioxide formed in reaction 6, and when 8 is superimposed on 6 it gives the net result of reaction 5.

The exact sequence by which combinations of part or all of these four reactions account for the formation of blue gas has been investigated by a number of workers but is still an unsettled question. Clement, Adams, and Haskins [30] concluded that, although both 5 and 6 occur, 5 is the dominant reaction and that the direction of

29 Segeler, C. G., *Fuel-Flue Gases*, Am. Gas Assoc., New York, 1939, p. 51.

30 Clement, J. K., Adams, L. H., and Haskins, C. N., *U. S. Bur. Mines, Bull.* **7** (1911), 58 pp

reactions 7 and 8 is towards the right. Gwosdz [31] studied the relative amounts of carbon monoxide and carbon dioxide obtained by action of steam on arc-light carbon with 0.1 percent ash and on charcoal with 1.4 percent ash, and decided that even at temperatures as low as 600° C no carbon dioxide is formed by reaction 6 but that the carbon dioxide comes from reaction 5 followed by 7. He found that much more carbon dioxide was formed with charcoal and thought that it comes from reaction 7 being catalyzed by the ash of the charcoal. Taylor [32] agreed with Gwosdz that 5 is the main reaction and that carbon dioxide comes mainly from reaction 7 accelerated by the catalytic action of the ash, particularly its iron oxides. Kohn [33] made a mathematical study of the gas-volume relations of the data of Bunte and Harris [34] and decided that the sequence of the reactions is 6 followed by the reverse of 7 at lower temperatures and 6 followed by 8 at the higher temperatures. He concluded that reaction 5 does not take place at all, differing from other writers.

There are, therefore, individual backers for almost all the possibilities, and the conclusions of Haslam, Hitchcock, and Rudow,[35] based upon their study of the action of steam on two kinds of carbon at temperatures from 650° C (1,202° F) to 1,200° C (2,192° F) and with a threefold change in steam pressure, help complete the list. They decided that 5, 6, and 8, all taking place monomolecularly at the sur-face of the carbon, are the essential reactions. Since these investigators found that changing the steam pressure from 360 millimeters of mercury absolute to 1,120 millimeters had practically no effect upon the relative proportions of carbon monoxide and carbon dioxide, they concluded that reaction 7, in which the equilibrium would be disturbed by an increase in the concentration of steam, takes place in the gas space only to a nearly negligible extent. These investigators also attempted to determine the relative rates of the reactions and claimed that at temperatures below about 900° C (1,652° F) reaction 5, which forms carbon monoxide directly, is practically nonexistent and that at these lower temperatures reaction 8, which forms carbon monoxide indirectly, has a rate twice as great as reaction 6, which forms carbon dioxide directly. It was thought that, at temperatures above about 900° C (1,650° F), reactions 5 and 6 proceed at equal rates and that reaction 8 has a rate 2.18 times as fast.

The work of Haslam and associates [35] using a 10-inch bed of 5- to 8-millimeter (⅕- to ⅓-inch) fuel also indicated that the ratio of carbon monoxide to carbon dioxide is closely related to the percentage of steam undecomposed. The curve in Fig. 5 based upon their results at temperatures of 1,652° F (900° C), 1,832° F (1,200° C), 2,012° F (1,000° C), and 2,192° F (1,200° C) shows that the ratio of carbon monoxide to carbon dioxide is substantially constant at 1.5 to 1 as long as the undecomposed steam is above 60 percent. As the undecomposed steam decreases below 60 percent the ratio carbon monoxide/carbon dioxide increases rapidly to 2.0 at 50, 3.5 at 40, 6.0 at 30, 11.0 at 20, and 20.0 at 14 percent, respectively, of undecomposed steam.

[31] Gwosdz, J., *Z. angew. Chem.*, **31**, 137–40 (1918).
[32] Taylor, H. S., *Fuel Production and Utilization*, D. Van Nostrand Co., New York, 1920, pp. 149–55.
[33] Kohn, S., *Ind. Eng. Chem.*, **14**, 69–72 (1922).
[34] Bunte, H., *J. Gasbeleucht.*, **37**, 81–6 (1894).
[35] Haslam, R. T., Hitchcock, F. L., and Rudow, E. W., *Ind. Eng. Chem.*, **15**, 115–21 (1923).

Pexton and Cobb [36] used a fuel bed 1 inch in diameter by 3 inches deep and particles of fuel from 0.1- to 0.2-inch size. They used three fuels: byproduct metallurgical coke, and coke made at 2,318° F by the volume of free space in the fuel bed independently of whether that steam supply is diluted with nitrogen or not"; and that "differently prepared cokes from the same coal do not react at the same
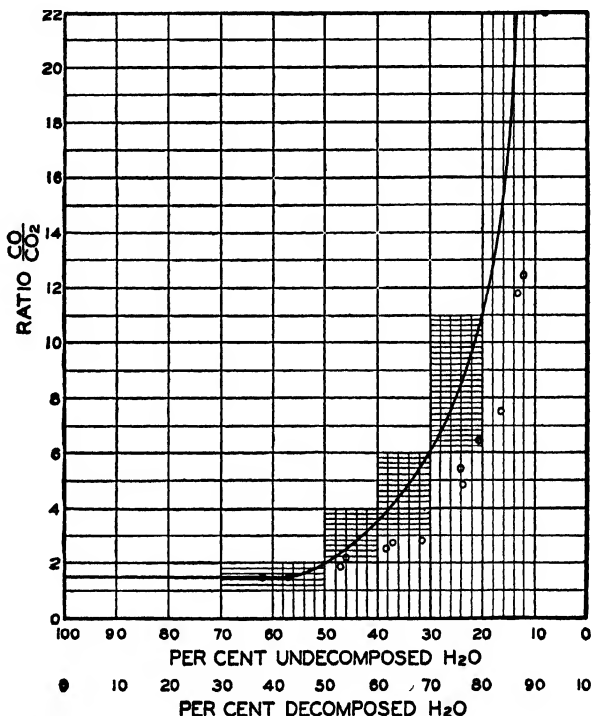
FIG 5. Ratio of carbon monoxide to carbon dioxide as a function of the percent undecomposed steam in the water-gas process. (From data of Haslam, Hitchcock, and Rudow [35] and Pexton and Cobb.[36]) Courtesy McGraw-Hill Book Company.

(1,270° C) and 1,652° F (900° C). By dilution with nitrogen, they varied the partial pressure of the steam and the time of contact. They reached the general conclusions that "the effectiveness of steam decomposition in a fuel bed of fixed dimensions and given temperature is determined by the rate of steam supply divided

ratio with steam, or accelerate to the same extent gas reactions proceeding at their surface." They believed that, whereas, in laboratory experiments, with a fair time of contact equilibrium may be reached, in practical operation the larger voids allow more steam to pass through without entering the gas film on the surface of the carbon where equilibrium is established in a very short time. The final product in

36 Pexton, S., and Cobb, J. W., *Gas J.*, 167, 161–9 (1924); *Gas World*, 80, 675–8 (1924).

practice is really gas high in carbon monoxide mixed with excess steam, and the securing of good-quality water gas is dependent upon the fact that equilibrium in the gas phase is not reached. The data of Pexton and Cobb for byproduct coke at 1,832° F (1,000° C) are plotted as points in Fig. 6. The best curve drawn through these points would show ratios of carbon monoxide/carbon dioxide of 1.7 at 50, 2.3 at 40, 3.6 at 30, 6.5 at 20, 12.0 at 12, and 22.0 at 8 percent of undecomposed steam, thus differing from the individual ratios obtained by Haslam, Hitchcock, and Rudow but showing a similar general relation between the percentage of undecomposed steam and the ratio of carbon monoxide to carbon dioxide in water gas.

Pexton and Cobb believed that the reaction of steam with carbon was of zero order and in this were in agreement with the indications of Thiele and Haslam [37] in results for three of their four types of carbon. Thiele and Haslam found that for activated carbon, for natural graphite and arc-electrode carbon at all temperatures investigated, and for retort carbon above 1,850° F (1,010° C) the reaction rate was independent of changes in steam pressure which indicated a zero-order reaction. They believed that the reactions might be:

(10) $C \text{ (bare)} + 2H_2O = 2H_2 + C_xO_y$

(11) $C_xO_y = C \text{ (bare)} + CO_2$

(12) $C \text{ (bare)} + H_2O = H_2 + CO$
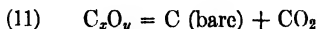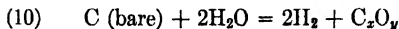
Reaction 11 was assumed to be slower than reaction 10, so that the rate of direct carbon dioxide formation was controlled by reaction 11. In many cases reaction 12 was supposed to be less important than reaction 10 because most of the surface is covered by the complex C_xO_y. If reaction 12 is negligible, then 11 predominates, and the reaction is of the zero order with respect to steam.

Brender à Brandis and Le Nobel [38] investigated the action of steam on charcoal, British and German coals, and retort carbon. They found the beginning of steam decomposition to be 1,067° F (575° C), 1,292° F (700° C), 1,517° F (825° C), and 1,580° F (860° C) for the four fuels, respectively. In all cases the first gas obtained was composed of one-third carbon dioxide and two-thirds hydrogen, which led them to conclude that the reactions for the formation of blue gas are 6 followed by 8.

More recent work has attempted not only to determine the primary products of the reaction of steam with carbon but also to explain the mechanism by which the oxygen of the water vapor combines with the carbon of the hot fuel. In order to understand the discussion of this work it is necessary to review briefly some ideas which have been developed regarding the changes which take place in the formation of coke from coal and the structural arrangements of the atoms of carbon and other elements in the resulting coke. It has been well substantiated by X-ray studies that in graphite the carbon atoms are arranged in regular hexagons which lie in planes. These planes are relatively far apart so that there exists a layered lattice structure.[39] Hydrogen and other foreign atoms attach themselves to the interlayer valences of the graphitic carbon. These other atoms may also be attached to the carbons at the edges of the graphite layers.

[37] Thiele, E. W., and Haslam, R. T., *Ind. Eng. Chem.*, **19**, 882–7 (1927).

[38] Brender à Brandis, G. A., and Le Nobel, J. W., *Het Gas*, **47**, 37–47 (1927) ; *Gas- u. Wasserfach*, **70**, 792–3 (1927).

[39] Blayden, H. E., and Riley, H. L., *J. Soc. Chem. Ind.*, **54**, 159-63T (1935).

From his study of coke formation Riley [40] concluded:

In the early stages of the pyrolysis of an organic substance the process of aromatic condensation begins, involving the formation of progressively larger polycyclic structures. The large flat molecules so produced arrange themselves in a multitude of minute, layered structures, not unlike small graphite crystallites, and there is evidence that in the case of cokes prepared at relatively low temperatures they still have hydrocarbon radicals bonded to the border carbon atoms of their hexagon planes. Foreign atoms such as hydrogen, oxygen, nitrogen, and sulfur play definite roles in these structures for they are only eliminated when the coke is heated to extremely high temperatures.

Sihvonen [41] and others have hypothesized that oxygen may be attached to the edge of a hexagon plane in two different ways. First the oxygen may be attached by two valence bonds to one of the edge carbon atoms in the ketone structure $>$C=O. Second, the oxygen may be attached to a carbon atom which itself is bonded to only one edge carbon atom. This gives the ketene structure $>$C=C=O and might occur if the oxygen came into contact with a carbon atom which was the remanent of a hexagon that had been disrupted by a reaction involving part of its six carbon atoms, or more probably by a carbon monoxide molecule attaching itself to a carbon of an edge hexagon. The ketene structure should be the weaker of the two, with a tendency for carbon monoxide to break off.

In his first experiments on the water-gas reaction, Sihvonen [42] used a rapid flow of highly rarefied cold water vapor with an electrically heated, pure, superficially porous graphite filament. The sole oxidation product at 1,450° C (2,640° F) was carbon monoxide, the yield of which increased rapidly above that temperature. The small rate of formation of carbon monoxide below 1,450° C is probably accounted for by the irreversible decomposition of the α-diketo groups on the corner carbon atoms of the graphite edges.[43] The rapid increase in carbon monoxide formation above 1,450° C was associated with a heat of activation of about 90 kilocalories. Thus the desorption of the single keto groups both in water vapor and in carbon dioxide is a reaction of the zero order,[44] with an activation energy of nearly 95 kilocalories as long as the edge parts of the graphite surface remain saturated with keto groups.[45] Meyer [46] confirmed the experimental basis of the keto-group theory.

Sihvonen [42] also studied the formation of blue gas in the reaction of a rapid flow of water vapor at 0.0001 millimeter mercury pressure, preheated by passing through a heated platinum band, and then led over a hot graphite filament. The flow of the water vapor was so rapid that measurable amounts of secondary carbon dioxide from reaction of carbon monoxide with oxygen formed by the dissociation of water vapor at the heated platinum band could not be formed. When the preheater temperature was 1,100° C (2,010° F) and the graphite filament only 900° C (1,650° F), small amounts of nearly pure carbon dioxide were formed. With the platinum band

[40] Riley, H. L., *Gas World*, **109**, Coking Sect., 81–4 (1938).

[41] Sihvonen, V., *Fuel*, **19**, 35–8 (1940).

[42] Sihvonen, V., *Ann. Acad. Sci. Fennicae*, **A38**, No. 2, 3–34 (1933).

[43] Sihvonen, V., *Svensk Kem. Tid.*, **48**, 185–202 (1936).

[44] Sihvonen, V., *Z. Elektrochem.*, **40**, 456–60 (1934); *Suomen Kemistilehti*, **8B**, 21–4, 29–30 (1935).

[45] Sihvonen, V., *Am. Acad. Sci. Fennicae*, **A41**, No. 3 (1935), 80 pp.

[46] Meyer, L., *Trans. Faraday Soc.*, **34**, 1056–61 (1938).

cold, no measurable oxidation products were formed at this temperature. When the preheater temperature was 1,100° C and the filament was 1,000° C (1,830° F), traces of carbon monoxide were formed, in addition to carbon dioxide.

This formation of carbon dioxide as a primary product of the reaction of hot water vapor on heated graphite was attributed to the oxidation of ketene groups. Other experiments had led to the conclusion that, on the surface of graphite, saturated keto groups cannot be oxidized by water molecules, even preheated ones, but that unsaturated ketene groups on the glowing graphite surface are readily oxidized to carbon dioxide by preheated water vapor though generally not by cold water vapor.[47] Ketene groups appear as the absorption product of carbon monoxide molecules on the edge atoms of the graphite lattice. Since the intermediate stage during the keto-group desorption consists in the formation and desorption of ketene groups, the formation of primary carbon dioxide with preheated water vapor must occur through the temporary primary ketene groups on the glowing graphite surface. Thus, if there is a primary formation of carbon dioxide in highly rarefied preheated water vapor, it would be expected that the formation of primary carbon dioxide would occur also at normal water vapor pressures.

Sihvonen [41] has further attempted to determine whether carbon dioxide is likewise a primary product of the reaction of carbon with steam at atmospheric pressure. In this work he passed steam through a quartz tube of 0.43-inch (1.1-centimeter) diameter, which was heated by a preheater

6 inches (15 centimeters) long and a reaction furnace 9.5 inches (24 centimeters) long. The carbon (0.3 to 1.0 gram of sugar charcoal, 1.0 gram of graphite, or 0.02 to 0.05 gram of diamond) was introduced into the reaction zone of the tube in a porcelain boat. Temperatures of 1,292° F (700° C) and 1,472° F (800° C) with the sugar charcoal, 1,562° F (850° C) to 2,012° F (1,100° C) with the graphite, and 1,922° F (1,050° C) to 2,192° F (1,200° C) with the diamond were used. The resulting blue gas was collected over a saturated common salt solution and analyzed for oxygen, carbon monoxide, carbon dioxide, and hydrogen.

The results obtained by Sihvonen led him to the conclusions that the water-gas process

(1) generally produces carbon monoxide as a primary product; (2) may also produce carbon dioxide as a primary product by the action of activated water molecules and especially at moderate temperatures and at higher pressures; and (3) is accelerated by catalyzers [sodium carbonate which he mixed with the charcoal or graphite in some tests] which cause corrosion and in this way increase the active edge parts of the graphitic carbon.

After a careful study of Sihvonen's results, it seems that in this work the reaction of the large excess of steam with the primary products of the action of steam on the hot carbon has neither been eliminated in the experimental procedure nor given sufficient consideration in the interpretation of the results. It seems probable that with the small concentration of water molecules present in the experiments at low pressures Sihvonen did remove the excess steam and primary reaction products from the neighborhood of the heated filament rapidly enough to avoid the secondary reaction. However, it is believed that in

[47] Sihvonen, V., *Brennstoff-Chem.*, **17**, 281–5 (1936); *Am. Acad. Sci. Fennicae*, **A51**, No. 4 (1938), 40 pp.

the procedure followed with steam at normal pressure the reaction $CO + H_2O = CO_2 + H_2$ in the presence of the high concentration of excess steam makes it uncertain whether the carbon dioxide found is a primary product or not. This opinion is given support by the results of Mayers,[48] who noted in his study of the reaction rate of steam and graphite that at higher temperatures (1,830 to 2,100° F or 1,000 to 1,150° C) the ratio of carbon monoxide to carbon dioxide was nearly constant at a given temperature regardless of steam velocities; but that at the lower temperatures (1,560 to 1,830° F or 850 to 1,000° C) the ratio of carbon monoxide to carbon dioxide increased markedly with the increase in steam velocities. These observations appear to indicate that at the higher temperatures the ratio of carbon monoxide to carbon dioxide in the presence of the relatively high concentration of steam was controlled by the equilibrium in the reaction $CO + H_2O \rightleftharpoons CO_2 + H_2$ and that at these higher temperatures this reaction is sufficiently rapid for it to approach equilibrium in the gas phase before the products are carried out of the heated portion of the reaction tube. On the other hand, at the lower temperatures the steam and primary products were removed from the hot zone before equilibrium was approached, and the higher the steam velocity the farther short of equilibrium was the mixture when the reaction was stopped by the cooling of the gases. To determine the primary products of the reaction of steam at normal pressures on hot carbon it will probably be necessary to devise an experimental procedure in which the composition of the products is determined at the surface so that the reaction between

the primary products and the excess steam will be eliminated.

CATALYSIS IN REACTIONS OF STEAM WITH CARBON

Reference has been made to the belief of earlier workers [31, 32] that reaction 7 is catalyzed by the ash of the fuel. The effects of various added inorganic constituents on the gasification of coke by steam were seriously investigated by Marson and Cobb,[49] who used cokes made by adding 5 percent of different substances to a coal which without addition gave a "pure coke" with only 1.3 percent ash. Of the materials added, silica, alumina, and fireclay were practically without effect on the gasification with steam. On the other hand, cokes made with addition of calcium oxide or carbonate, iron oxide, and sodium carbonate exhibited a greatly increased activity in the decomposition of steam and in the percentage of carbon monoxide in the gas. When cokes made by carbonization at 1,470° F (800° C) were gasified with steam at 1,830° F (1,000° C) the percentages of steam decomposed with different steam rates were as follows:

STEAM RATE liters per hour	PERCENT OF STEAM DECOMPOSED BY			
	"Pure" Coke	CaO Coke	Fe_2O_3 Coke	Na_2CO_3 Coke
5	68	84	94	99
10	61	82	91	99
15	56	81	90	98
20	51	78	87	98

It is evident that sodium carbonate had the greatest catalytic effect. The action of this addition agent on the gasification of carbon with air and with carbon dioxide as well as with steam and mixtures of steam with oxygen has been studied extensively

48 Mayers, M. A., J. Am. Chem. Soc., 56, 1879–81 (1934).

49 Marson, C. B., and Cobb, J. W., Gas J., 175, 882–91 (1926).

by White and coworkers.[50] The catalytic influence of sodium carbonate in the gasification of carbon with air or carbon dioxide has been discussed in the section on producer gas (see pages 1603–6). The action of sodium carbonate in mixtures of steam and oxygen will be considered later. The work of Fox and White seems to indicate that the mechanism of the action probably involves the formation of sodium vapor according to the reaction

$$Na_2CO_3 + 2C = 3CO + 2Na$$
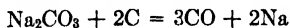
and the subsequent regeneration of the sodium carbonate by reaction of the sodium vapor with steam and carbon dioxide. White and Fleer have also indicated that sodium carbonate catalyzes the reaction of carbon monoxide with steam so that when it is present the gas has a composition closely approaching that required for equilibrium in reaction 7.

Work on catalysis of reaction 7, which is important in the use of blue gas as a source of industrial hydrogen, as reported by White and Shultz [51] may be summarized as follows: Catalysts made by the fusion of cobalt oxide would, when properly reduced in hydrogen, effectively catalyze the water-gas reaction to equilibrium at temperatures as low as 283° C and space velocities as high as 1,800. The addition of various promoters seemed capable of largely repressing the simultaneous formation of methane. Iron in quantities as high as 3 percent appeared to inhibit the formation of methane without cutting down appreciably the activity toward the water-gas reaction. Copper as a promoter gave promising results. A cobalt catalyst containing 38 percent copper was particularly active as a water-gas catalyst without synthesizing significant quantities of methane.

KINETICS OF REACTION OF STEAM ON CARBON

The rate of reaction of steam on carbon has been investigated by Mayers,[48] who measured the rate of oxidation of graphite by steam at atmospheric pressure at temperatures between 1,560 and 2,120° F (850 and 1,160° C) under conditions which eliminated the effect of diffusion as the rate-determining process. The criterion of the attainment of these conditions was that the steam-velocity coefficient of the observed rate of reaction should vanish.[52] The exposed surface of the graphite was treated to eliminate porosity as an uncertain factor in the determination of the area of the surface. Results showed that, in the high-temperature range of 1,830 to 2,120° F (1,000 to 1,160° C), the rate of gasification, G_1, of carbon in micromoles per square centimeter per second was given by

$$\log G_1 = 6.20 - (35,130/4.575T)$$

In the low-temperature range of 1,560 to 1,830° F (850 to 1,000° C), the gasification rate, G_2, was given by

$$\log G_2 = 8.42 - (49,720/4.575T)$$

Where T = absolute temperature in degrees Centigrade.

The reaction rates in pounds of carbon gasified per square foot per minute can be obtained by multiplying the values obtained for G_1 and G_2 in the formulas by 0.00147. In attempting to apply these values, however, it must not be overlooked that, in generator fuels, it is coke which reacts with the steam and that porosity greatly increases the surface of the coke.

[50] Fox, D. A., and White, A. H., *Ind. Eng. Chem.*, **23**, 259–66 (1931). Weiss, C. B., and White, A. H., *ibid.*, **26**, 83–7 (1934). Fleer, A. W., and White, A. H., *ibid.*, **28**, 1301–9 (1936).

[51] White, E. C., and Shultz, J. F., *ibid.*, **26**, 95–7 (1934).

[52] Mayers, M. A., *J. Am. Chem. Soc.*, **56**, 70–6 (1934).

Attempts have been made, as we have previously indicated, to determine the relative rates of reactions

(5) $C + H_2O = CO + H_2$

and

(6) $C + 2H_2O = CO_2 + 2H_2$
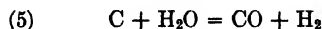
However, since it is probable that the equilibrium in the surface gas film of the reaction

(7) $CO + H_2O = CO_2 + H_2$
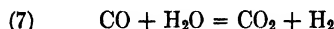
is what really determines the proportions of the gasified carbon which appear as carbon monoxide and carbon dioxide, it seems useless to consider the reaction rates of 5 and 6 independently.

EQUILIBRIUM IN BLUE-GAS REACTIONS

The composition of blue gas when equilibrium is attained at any temperature probably is controlled by equilibrium in the reaction 7

$$CO + H_2O = CO_2 + H_2$$
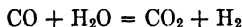
This equilibrium is reached extremely rapidly at high temperatures and may be approached closely in the gas spaces of the hotter parts of the fuel bed or in the gas film on the reacting surfaces of the carbon. In the gasification of fuel with steam, the reaction is largely on the surfaces of the carbon in the pores of the coke, and the gases held in these pores furnish an excellent opportunity for attainment of equilibrium of the steam with the primary products of the reaction. Equilibrium in reaction 7 alone will, therefore, be considered here.

Austin and Day [53] have discussed critically the values of the equilibrium constants in the various combustion equations.

[53] Austin, J. B., and Day, M. J., *Ind. Eng. Chem.*, **31**, 23–31 (1941).

The values chosen by them for reaction 7 are given in Table II. Since the values of

TABLE II

EQUILIBRIUM CONSTANTS FOR WATER-GAS REACTION [53]

Temperature		$K = \dfrac{(CO_2)(H_2)}{(CO)(H_2O)}$	$\dfrac{1}{K}$
°C	°F		
400	752	14.1	0.071
450	842	7.04	0.142
500	932	4.88	0.205
550	1,022	3.41	0.294
600	1,112	2.54	0.394
650	1,202	1.95	0.513
700	1,292	1.54	0.650
750	1,382	1.26	0.795
800	1,472	1.05	0.952
850	1,562	0.892	1.12
900	1,652	0.764	1.31
950	1,742	0.672	1.49
1,000	1,832	0.592	1.69
1,050	1,922	0.527	1.90
1,100	2,012	0.474	2.11
1,150	2,102	0.435	2.30
1,200	2,192	0.399	2.51
1,250	2,282	0.369	2.71
1,300	2,372	0.341	2.94

the reciprocal of K plot more conveniently than the values of K, these are also included in the table. The values given for K were calculated from spectroscopic data by Kassel.[54] The curve for $1/K$ may be carried to higher temperatures by means of the following:

°C	°F	$1/K$
1,371	2,500	3.24
1,482	2,700	3.70
1,593	2,900	4,18

These values are for the equilibrium constant of the reverse reaction calculated by means of the relation

$$\log_{10} K = -\Delta F°/4.579T$$

[54] Kassel, L., *J. Am. Chem. Soc.*, **56**, 1838–42 (1934).

where T is temperature in degrees K, from the values of the free energy change, $-\Delta F°$, for the reaction

$$CO_2 + H_2 = CO + H_2O$$
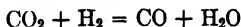
by the equation

$$\Delta F° = 10,100 - 1.81T \ln T + 0.00445T^2$$
$$- 0.00000068T^3 - 0.54T$$

In this equation of Lewis and Randall,[55] the integration constant, $-0.54T$, was obtained by consideration of the data of Hahn[56] and of Haber and Richardt[57] on the equilibrium constant of the water-gas reaction. The agreement of values for $1/K$ calculated from the Lewis and Randall free-energy equation with those from Kassel's later and precise work, from which the former values deviate only slightly at temperatures below 2,000° F, gives assurance in the use of the Lewis and Randall equation for the free-energy relations of the reaction.

REACTIONS IN GENERATOR FUEL BED

Unfortunately data to permit the determination of the sequence and relative importance of the various reactions in a blue-gas generator fire have never been collected. Work which helps to bridge the gap between the laboratory study of the reactions involved in the blue-gas process and their application on a large scale was reported by the American Gas Association Carbonization Committee in 1926.[58] In this work, cokes produced by carbonization of coal from the same mine in four different types of carbonizing apparatus were

tested for their relative utility as fuel for the manufacture of blue gas. These tests were made in a special apparatus with fuel bed 1.5 feet in diameter and 4.0 feet deep. Fresh charges of sized coke between 0.75 and 1.5 inches were used in each test. The cokes were compared, first, as to their ability to retain heat during the air blow at varying rates, and second as to their ability to decompose steam during the run. At low air rates, no significant differences in the heat retained in the fuel bed were observed. As the air rate was increased, the percentage of heat retained by the fuel bed decreased, this change being greatest for the denser cokes. The cokes did not show any marked variation in their reactivity to carbon dioxide. In their ability to decompose steam there was no indication of a significant difference which could be correlated with any physical property of the cokes.

Since little difference was found in the behavior of the various cokes, the results obtained for the byproduct oven coke made from a Pittsburgh Seam coal may be taken as typical. Some of these which might be useful in indicating trends in the reactions of the blue-gas generator are given in Table III.

It is evident that increasing the air rate by 1.9 fold nearly doubles both the rate of fuel consumption and the sensible heat in the blast gases. At the same time, it had little effect on the carbon monoxide in the blast gases after 1.5 minutes of blowing but decreased somewhat the percentage of heat stored in the fuel bed. Though these results seem to disagree with the previous statement that a high blasting rate would bring up the fuel-bed temperature with the use of less fuel, it must be remembered that no data are given here of the temperature in the fuel bed which would indicate the time for the termination of the

[55] Lewis, G. N., and Randall, M., *Thermodynamics and Free Energy of Chemical Substances,* McGraw-Hill Book Co., New York, 1923, 653 pp.

[56] Hahn, O., *Z. physik. Chem.,* **44**, 513–47 (1903), **48**, 735–8 (1904).

[57] Haber, F., and Richardt, F., *Z. anorg. allgem. Chem.,* **38**, 5–64 (1904).

[58] Haslam, R. T., Ward, J. T., and Boyd, J. H., Jr., *Proc. Am. Gas Assoc.,* **1926**, 1083–104.

TABLE III

DATA ON AIR BLOWS WITH 0.75- TO 1.5-INCH BYPRODUCT COKE IN A 4-FOOT FUEL BED
AT INITIAL TEMPERATURE OF 1,740° F [58]

Time in Minutes	Gas Analysis			Heat Distribution, Percent in Fuel Losses			Pounds Carbon per Square Foot per Minute
	CO_2	O_2	CO	Bed	CO	Sensible	
Air rate = 122 cubic feet per minute per square foot; pressure = 2.2 inches water							
0.42	16.6	1.2	5.0	75.2	16.2	8.6	0.89
0.99	13.8	0.2	11.6	60.0	32.1	7.9	1.03
1.59	10.2	0.4	17.6	48.0	44.5	7.5	1.17
2.19	8.4	0.4	21.4	42.3	50.5	7.2	1.30
3.42	6.0	0.4	24.8	36.2	56.5	7.3	1.36
Air rate = 233 cubic feet per minute per square foot; pressure = 11.2 inches water.							
0.39	20.2	0.6	0.4	80.3	1.4	18.3	1.54
0.88	18.6	0.4	3.6	70.8	11.3	17.9	1.68
1.68	12.0	0.0	17.3	44.6	41.4	14.0	2.41
2.35	8.8	0.0	21.0	35.8	49.4	14.8	2.42
3.35	5.4	0.2	26.2	27.5	58.0	14.5	2.65

blow. The temperature of the blast gases at the top of the fuel bed after 3.4 minutes of blowing with 122 cubic feet of air per minute per square foot was only 605° F as compared with a temperature of 955° F after 0.9-minute blasting with 233 cubic feet per minute per square foot. With the shorter time and higher blasting rate there was only 3.6 percent of carbon monoxide in the blast gases, and 70.3 percent of the heat was stored in the fuel bed, as compared with 24.8 percent of carbon monoxide and only 36.2 percent of heat in the fuel bed with the longer time and lower blasting rate.

It is evident from Table IV that with this depth of fuel bed and the conditions of blasting specified it would not be practical to continue the steam run longer than about 1.5 minutes with the higher steam rate, or longer than about 2.5 minutes with the lower steam rate. If the accuracy of the gas analysis is assumed to be within ±0.2 percent for the carbon dioxide and

oxygen and ±1.0 percent for the carbon monoxide and hydrogen there appears to be evidence from a hydrogen balance that at the lower steam rate some methane

TABLE IV

DATA ON STEAM DECOMPOSITION WITH 0.75- TO 1.5-INCH BYPRODUCT COKE IN 4.0-FOOT FUEL BED AFTER BLASTING 5 MINUTES WITH AIR AT 218 CUBIC FEET PER MINUTE PER SQUARE FOOT [58]

Time in Minutes	Gas Composition					Percent Steam Decomposed
	CO_2	O_2	CO	H_2	CH_4	
Steam rate = 2.06 pounds per square foot per minute.						
0.43	2.4	0.6	43.6	46.7	0.0	
1.18	3.5	0.4	43.8	49.4	...	57
1.91	5.6	0.4	41.2	50.6	...	48
2.68	8.2	0.5	38.4	50.9	...	36
3.72	11.0	0.6	32.7	52.7	...	31
4.85	13.6	1.2	27.9	54.5	...	20
Steam rate = 4.29 pounds per square foot per minute.						
0.50	3.2	2.8	38.7	51.0	1.8	68
1.30	5.5	2.4	37.8	49.5	1.9	52
2.84	11.8	1.0	29.2	53.9	0.6	28
3.83	14.4	0.1	26.7	52.7	1.5	18
4.55	14.7	0.5	26.8	55.0	1.2	15

should have been found in the gas after 2.68 minutes' run, and that, at the higher steam rate, considerable hydrogen in the gases at 0.50 and 1.30 minutes came from steam, the oxygen of which either appeared in the free oxygen reported or was retained by the coke in a solid carbon-oxygen complex.

STEAM DECOMPOSITION IN PRACTICE

A good economical blue gas with coke fuel has the following percentage composition and calorific values: [59]

CO_2	CO	H_2	CH_4	N_2	H_2S	Btu/cu ft
6.0	38.5	50.5	1.0	3.5	0.5	300

Theoretically 25 pounds of steam must be decomposed to make 1,000 cubic feet of this gas; in practice, the figure is 45 to 50 pounds or more. The use of 100 percent or more of steam in excess of the amount theoretically needed not only results in losses from the heat carried away and the additional raw material required, but also, as has been indicated, decreases the ratio of carbon monoxide to carbon dioxide in the gas and may sometimes point to bad fuel-bed conditions. On the other hand, according to Huff,[60] "a large quantity of excess steam is ordinarily used and deemed necessary in order to secure satisfactory clinker conditions and capacity. It may be questioned, however, whether all the excess steam is necessary or desirable."

Although some idea of the amount of undecomposed steam, as well as of fuel-bed conditions, can be obtained from the percentage of carbon dioxide in the blue gas, it would be better to have a reliable method of determining the percentage of undecomposed steam directly. At least three methods of doing this have been developed and applied with some degree of success. The Benesh steam-decomposition meter [61] utilizes the principle of the wet- and dry-bulb thermometers to measure the amount of undecomposed steam in the gas. In the Koppers steam-decomposition meter [62] the decrease in the pressure on the gas caused by the condensation of the water vapor in it serves as an indication of the undecomposed steam. A steam-decomposition meter which utilizes rotameters to measure the volume flow rate of the gas before and after condensation of the undecomposed steam has also been designed [63] and its performance at the Belle, W. Va., works of the du Pont Company has been described.

The Benesh steam-decomposition meter has been discussed by Carter,[64] who presented charts to bring out the following points:

1. If the steam rate was kept constant during each run, decreasing the rate from 220 pounds per minute (220/71 = 3.1 pounds per square foot per minute) during one series of runs to 192 pounds per minute during another series of runs increased the average steam decomposition from 57 to 65 percent.

2. If the steam rate was decreased during the same run, starting with 192 and decreasing to 168 and then to 160 pounds per minute, as the run progressed the average steam decomposition became 70 percent.

3. When the up-run (about 45 percent of the total run) was placed first in the

[59] Pacific Gas Assoc., *Gas Engineers' Handbook*, McGraw-Hill Book Co., New York, 1934, p. 283.

[60] Huff, W. J., *Proc. Am. Gas Assoc.*, **1929**, 1257–9.

[61] Benesh, M. E., *Proc. Am. Gas Assoc., Tech. Sessions*, **1921**, 9–38.

[62] McGurl, G. V., Nordmeyer, G. J., Blackwood, O. H., Exline, P. G., and Doherty, J. D., *Proc. Am. Gas Assoc.*, **1931**, 1174–97.

[63] Putnam, W. J., and Moses, D. V., *Am. Gas Assoc. Monthly*, **23**, 112–6 (1941).

[64] Carter, W. B., *Proc. Am. Gas Assoc.*, **1929**, 1275–82.

cycle the percentage of steam decomposed decreased rapidly from above 90 at the beginning to about 60 at the end of the up-run.

4. When the back-run (54 percent of the total run) followed the up-run the average figure obtained for steam decomposition during the back-run ranged from about 35 to 45 percent, depending upon the steam rate. Even when the back-run was placed ahead of the main up-run and preceded only by a 3-second steam purge, the average figure obtained for the steam decomposition during the back-run was only 52 to 53 percent.

5. The percentage of undecomposed steam in the back-run gas was greatest at the beginning of the back-run even when the back-run was placed ahead of the up-run. This was thought to be because the gas as it left the bottom of the fuel bed picked up moisture which had condensed

in the ash pan or which resulted from leaks in the water-cooled crusher section of the automatic grate. It seems probable, therefore, that the figures obtained for the steam decomposition during the back-run were lower than those which represented the true percentage of steam decomposed in the fuel bed during this portion of the cycle.

The chart reproduced in Fig. 6 [65] shows steam-decomposition curves constructed from data obtained with the Koppers steam-decomposition meter. These curves also show the decrease in percentage of steam decomposed as the run progresses. The dips in the curve at the point of change from up-run to down-run, and vice versa, were probably caused by the steam below or above the fuel bed when the change was made. The curves in the chart

[65] See p. 1184 of ref. 62.

Curves taken One Hour apart
No. 2 taken just before Shutting Down
Thinner Fuel Bed than No.1
Same Steam Rate
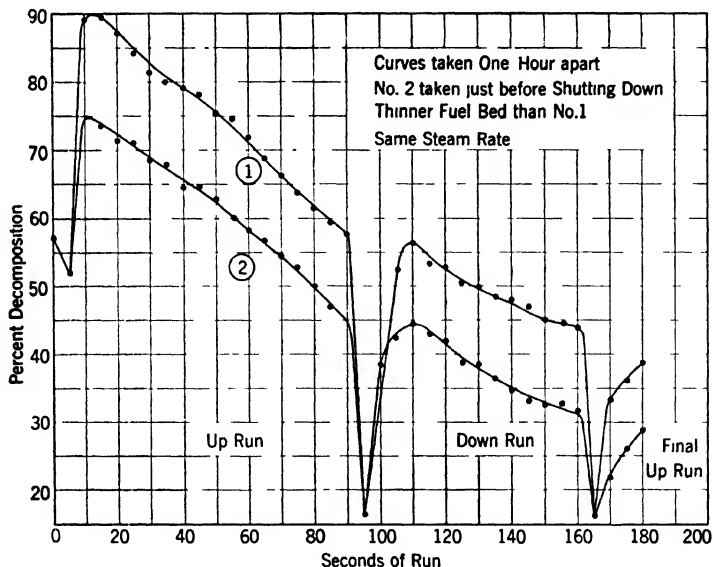
FIG. 6.   Steam decomposition in the carburetted-blue-gas generator as measured by the Koppers steam-decomposition meter.[65]

bring out increased steam decomposition in a thicker fuel bed.

FORMATION OF METHANE IN BLUE GAS

Analyses of blue gas, even of that made from coke, show small amounts, usually about 1 percent, of methane, which is probably formed by the reaction

$$(13) \quad CO + 3H_2 = CH_4 + H_2O$$
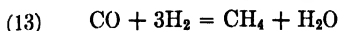
Possibly at the higher temperatures some methane is formed by:

$$(14) \quad CO_2 + 4H_2 = CH_4 + 2H_2O$$
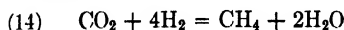
Both these reactions are exothermic, and, since 14 evolves less heat than 13, it would be favored over 13 by increased temperature. Meade [66] stated that the methane in blue gas probably comes mostly from distillation of tacky coke, but it seems doubtful that this could account for the methane found in blue gas made from screened byproduct coke. The methane found in the analysis of the blue gas from coke in the experimental work cited on page 1706 cannot be accounted for by the 0.4 percent of hydrogen shown by analysis of the coke. Reaction 13, which is catalyzed by nickel at 575° F (300° C), has been proposed as a method of lowering the carbon monoxide content of city gas and at the same time increasing its heating value. Since this reaction is exothermic, the total amount of heat available in the gas containing methane made by this process would be less than that in the blue gas from which it was made.

RAW MATERIALS FOR BLUE GAS

In addition to the air for blasting the fuel bed and the steam decomposed in the gas-making runs, the material used in the manufacture of blue gas is a solid fuel high in carbon. In the earlier days, the solid fuel was either anthracite or coke. Later difficulties in obtaining coke under war conditions led to attempts to substitute bituminous coal, and as the operating troubles with this fuel were overcome it became largely a question of which fuel was most economical.

It has been shown in previous discussions that when steam is used in the manufacture of producer gas the resulting gas is really a mixture of producer gas and blue gas made by a continuous process. Considerable work has been done on the problems of substituting oxygen or a rich mixture of oxygen with nitrogen for the air used in the producer. In this process it is proposed to pass a mixture of steam and oxygen through a generator and thus produce continuously a gas which is a mixture of blue gas and carbon monoxide.

ANTHRACITE

Anthracite generally used in the manufacture of blue gas is broken, or egg, size. Standard specifications for these grades of anthracite are as follows: [67]

MAXIMUM ALLOWABLE PERCENTAGES

GRADE	Under Size	Over Size	Slate	Bone	Total Impurities
Broken, 3¼ in. by 4½ in.	10	5	1	2	3
Egg, 2⁵⁄₁₆ in. by 3¼ in.	10	5	2	2	4

As shown in Table V, the ash content is usually around 10 percent. To be suitable for the manufacture of blue gas, anthracite should have as low a percentage as is possible of ash with a moderately high fusing point and should consist of large lumps with a minimum proportion of fines.

Where it is available at a fair price, an-

[66] Meade, A., *Modern Gas Works Practice*, Benn Bros., London, 1921, p. 698.

[67] Holbrook, E. A., and Fraser, T., *U. S. Bur. Mines, Bull.* 234 (1925), p. 115.

TABLE V

Analyses of Fuels for Manufacture of Blue Gas

Kind of Fuel	Moisture as Received	Analysis on Dry Basis					Ash-Fusion Point ° F	Size of Fuel inches
		Volatile Matter	Fixed Carbon	Ash	Sulfur	Btu per Pound		
Anthracite, Pittston broken coal *	4.51	6.07	83.94	9.99	0.91	......	2,600+	3⅞₆ to 4⅞₆
Anthracite, broken †	3.30	5.23	81.74	13.03	0.91	13,042	....	....
Anthracite, broken †	3.55	5.27	84.90	9.83	0.78	13,561	....	....
Anthracite ‡	2.77	5.44	84.19	10.37	0.86	12,830	....	....
Water-gas coke §	3.56	1.93	89.76	8.31	0.60	......	2,300 and above	Over 2-in. grizzly
Horizontal and inclined retort coke †	10.09	1.91	87.92	10.17	0.73	12,746	....	....
Horizontal and inclined retort coke †	0...	2....	00.00	4...	0...	10,...	....	....
Byproduct oven coke †	3.13	1.99	89.17	8.84	0.63	13,081	....	....
Water-gas coke ‡	3.95	2.15	87.36	10.49	0.93	......	2,190	....
Water-gas coke ‡	1.67	2.21	87.32	10.47	1.11	13,004	2,678	....
Spokane gas-house coke ‖	1.30	8.3	70.3	21.3	....	11,150	....	....
Denver gas-house coke ‖	....	2.88	79.58	17.54	0.62	11,899	....	....
Boone-Chilton coal ¶	1.82	36.48	58.73	4.79	0.56	14,380	2,825	....
Fairmont gas coal, average **	1.06	34.67	58.16	7.17	1.00	......	....	3 to 6
Elkhorn gas coal **	1.94	37.77	59.11	3.12	0.54	14,750	....	3 to 6
Perry County, Ill.††	7.77	36.72	53.45	9.83	1.40	12,816	....	....
Franklin County, Ill.‡‡	7.95	36.08	53.71	10.21	1.31	......	....	6 × 3 lump
Whatcom County, Wash., subbituminous coal ‖	8.01	43.44	37.23	19.33	0.35	10,760	....	Washed pea size
Portland lampblack briquets ‖	3.40	9.0	90.7	0.3	....	15,100	....	....

* E. C. Uhlig, average of 108 samples.
† C. A. Lunn, each is average of a number of shipments.
‡ A. F. Kunberger.
§ E. C. Uhlig, average of 323 samples of Seaboard coke for 1924.
‖ *Proc. Pacific Coast Gas Association*, 1925, 448.
¶ Boone County Coal Corporation, pamphlet on water-gas-generator fuel.
** The Consolidation Coal Co., pamphlet on gas and byproduct coals, and private communication from W. D. Barrington, Consulting Sales Engineer.
†† Used in Streator tests, Odell, W. W., and Dunkley, W. A., *U. S. Bureau of Mines, Bull.* 203, 76 (1924).
‡‡ *Report of A. G. A., Water Gas Committee, 1925*, p. 21.

thracite is an excellent fuel for the manufacture of blue gas. It is the densest, most concentrated form of commercial carbon, which gives a greater weight of fuel in the fuel bed and permits more heat to be stored up in the fire during the blow. This results in a high capacity from the generator when using anthracite. Anthracite has, however, the disadvantage of increasing price and of a trend towards higher ash content. Labor troubles which in the past have rendered the supply undependable have also encouraged the utilization of other fuels in the manufacture of blue gas.

COKE

Coke for the production of blue gas should have the same ash characteristics that have been stressed for anthracite, namely, the amount of ash should be small

and its fusing point should be fairly high. Since the amount and nature of the ash in coke depend upon the ash characteristics of the coal from which it is made, it follows that coke for blue-gas manufacture should be made from carefully selected coals. It is not always possible to control the amount and nature of the ash in coke used for making blue gas, as, for instance, where the coke from gas retorts is used in carburetted-blue-gas generators, but even so the effects of the amount and nature of the ash in the coke on the operation of the blue-gas generators should be given as much weight as possible in the selection of the coal for the carbonizing plant.

In respect to size, coke for making blue gas should be uniform lumps and free from fines. Egg coke (1⅞ to 2½ inches) or larger is suitable. When coke is purchased for the manufacture of blue gas, a special size is often specified and designated as water-gas-size coke. This, for byproduct coke, is run-of-oven coke over a 2- or 2½-inch rotary grizzly. When coke from a carbonizing system is used for making blue gas in the same plant, it is customary to take the coke as it comes after screening out the breeze under ½- or ¾-inch size. It has also been proposed to charge hot coke into the blue-gas generators as it comes from the carbonizing apparatus without screening.

With regard to the other characteristics which make one coke more suitable than another for the manufacture of blue gas, though there is no lack of arguments and sales talk on the merits of the different kinds of coke, authoritative information on the subject is scant. It is claimed by those interested in selling this kind of coke that screened beehive-oven coke made from a washed coal is superior to other cokes for making blue gas. In addition to the smaller amounts of ash and sulfur in this coke on account of the preparation of the coal, a greater density and less pore space are claimed as special advantages. On the other hand, it has been stated [68] that medium-sized porous coke is to be preferred to large hard coke such as that used for blast furnaces. A dense hard coke permits a greater weight of fuel to be contained in the generator and by its resistance to breakage in handling gives a smaller proportion of fines and a freer passage for the gases. These factors working together might result in a greater capacity for a given blue-gas apparatus. On the other hand, it is likely that a more porous coke may be more reactive and combine faster with the air and steam, giving a higher capacity.

The reactivity of the coke has been thoroughly studied in connection with its use in iron blast furnaces. Several methods have been advanced for the determination of reactivity in the laboratory,[69] but so far it has been impossible to obtain a definite relationship between the results of laboratory tests and operating results in the blast furnace. Although a connection has been thought to exist between the reactivity of coke and its suitability for blue-gas manufacture, no definite relations have been established. So many variables influence the results obtained from a fuel in a blue-gas generator, including in addition to those mentioned above the possible catalytic influence of the chemical nature of the ash, that it is extremely difficult to determine the effect of such a factor as the porosity or the reactivity of different cokes. The investigation of the American Gas Association Carbonization Committee on the blue-gas-making properties of coke made from

68 Davidson, W. B., *Gas Manufacture*, Longmans, Green and Co., London, 1923, p. 261.

69 Fieldner, A. C., *Chem. & Met. Eng.*, 29, 1052–7 (1923). See also Chapter 24.

the same coal by five different types of carbonizing apparatus has already been referred to, and it was pointed out that no significant differences which could be correlated with any known physical property were found. In this connection it must be remembered that high reactivity to carbon dioxide during the blow is usually coupled with greater ability to decompose steam during the run. The latter is an advantage in blue-gas fuel; the former is not. This observation is confirmed by work of Fox and White,[50] who showed that the great increase in the reactivity of coke to both steam and carbon dioxide, which is caused by the addition of sodium carbonate, is of no advantage in the present type of blue-gas apparatus. (See also Chapter 24.)

Compared with anthracite, coke is more bulky, and hence the capacity of the blue-gas apparatus is often less with coke. This generalization, however, does not invariably hold, and some operators think that the greater reactivity of coke accounts for the fact that with certain byproduct oven cokes they have obtained even greater capacity in carburetted-blue-gas sets than with anthracite. Coke has the advantages that it does not crack or crumble during combustion and that its porous structure exposes more surface to the action of the air and steam.

BITUMINOUS COALS

The use of bituminous coal in blue- and carburetted-blue-gas generators dates from the necessity during 1917-8 of finding in the Illinois district a substitute in water-gas manufacture for coke which the restrictions of the War Fuel Administration made it impossible to obtain. Since then the developments in its use have proved that bituminous coal has certain advantages as a blue-gas-generator fuel even in

normal times. In many parts of the country there are no local supplies of good coking coals or of anthracite. In such sections the possibility of using low-priced local high-volatile coals instead of expensive coke or anthracite which must be shipped long distances is financially attractive. The results of an extensive investigation on the subject are discussed in different publications of the U. S. Bureau of Mines [70] and in convention reports of the American Gas Association.

The main difficulties encountered in the use of bituminous coal in water-gas sets are: (1) reduced capacity caused by trouble in keeping the fire in good condition; (2) stopping up of the checkerbrick in the carburetter and superheater with fine fuel carried over by the blast, preventing the use of high blast pressure in an attempt to bring up the capacity of the set; and (3) smoke resulting from incomplete combustion of the tarry volatile matter from the coal when blasted after fresh fuel was charged on the fire.

The difficulty of keeping the fire in good condition was solved by the pier process.[71] It was noticed that when a coking bituminous coal was the generator fuel the activity was mainly located at the periphery of the fire, and the central portion was relatively dead. The high temperature and radiated heat from the hot fireclay walls caused a rapid coking and shrinkage of the fuel which allowed most of the air and steam to pass up near the walls, resulting in a further opening up of the fuel bed along the walls. On the other hand, the matting of the fuel caused by the plastic state in the center of the fire offered increased resistance to the blast and steam

70 Cf. Odell, W. W., and Dunkley, W. A., U. S. Bur. Mines, Bull. 203 (1924), 92 pp.

71 Novak, M. P., Proc. Am. Gas Assoc., 1925, 1194-202.

and resulted in a larger proportion of the activity being limited to the area along the walls. The tendency of the lumps of fuel to roll to the sides and leave the fines in the center during charging further augmented this condition.

In the pier process a cylindrical pier of refractory material introduced into the center of the fuel bed extends up almost to the top level of the fuel. This results in coring out the inactive central portion of the fire, and by the effect of the additional radiating wall surface another ring of activity extends outward from the pier. By a proper pier design for a given coal the two rings can be made to merge and give a fire of practically uniform activity. The clinker then formed is almost flat, having about the same height at the pier wall as at the outer wall with only a slight dip near the center of the annular ring. With the permeability and temperature uniform across a horizontal section of the fuel bed, which are the conditions of good operation with coke, a material increase in capacity and fuel economy is obtained. A pier in a water-gas generator is shown in Fig. 7. For an 11-foot generator with a grate diameter of 9 feet the diameter of the pier may be 3 feet. This gives an annular ring 3 feet wide so that no portion of the fuel bed is more than 18 inches from a radiating refractory wall. For smaller generators the diameter of the pier might be somewhat less than one-third of the grate diameter and vary according to the fuel characteristics. The reduction of grate area resulting from the introduction of the pier in an 11-foot generator was 11.1 percent, but the gas-making capacity was increased as much as 62 percent with a corresponding improvement of 10 to 13 percent in fuel economy.

Another device designed to eliminate the dead center in the generator fire with bitu-minous coal is the water-cooled steel air and steam nozzle described by Paff.[72]

The stopping up of checkerbrick by fine fuel blown over in the blast and the smoke caused when bituminous coal is the generator fuel are troubles peculiar to the carburetted-blue-gas process and will be treated in a later section. No smoke should be caused by bituminous coal in the manufacture of blue gas, for the smoke-forming components can be completely burned by the air used in the combustion chamber ahead of the waste-heat boiler.

The composition of high-volatile coals for making blue gas depends upon the locality and is fairly represented by the data in Table V. In the northern Pacific Coast states, high-volatile coals which are not suitable for carbonization have been found successful in the back-run process of making carburetted blue gas. In the eastern states, high-grade bituminous coals with low sulfur and high-fusing ash are active competitors of coke and anthracite for blue-gas-generator fuel. It is claimed that the coal from Boone County, W. Va., whose analysis is given in Table V, is used in more than 70 carburetted-blue-gas plants. The results of the work thus far done to evaluate bituminous coals as blue-gas-generator fuel show [73] that chemical analysis is valuable only in fixing the limits of moisture, sulfur, and ash, that a modified shatter test may be successful in predicting the degradation in handling, and that plasticity and agglutinating-power tests might be developed to aid in predicting the behavior of bituminous coals in the generator. So far, plant tests have been the only successful means of evaluating bituminous coals for blue-gas manufacture. A list of 36

72 Paff, J. N., *Gas Age-Record*, **63**, 605–6 (1929).
73 Pettyjohn, E. S., *Proc. Am. Gas Assoc.*, **1930**, 1535–63.

Fig 7   Pier in U G I water gas generator

coals which have given good results in blue-
or carburetted-blue-gas apparatus was re-
ported at the 1929 convention of the
American Gas Association   Bituminous
coals are used in blue- or carburetted-blue-
gas generators in various mixtures with
coke and anthracite or alone. When used
alone, except in the pier process, there is
a decided loss in capacity in the larger sets
as compared with the capacity with coke
or anthracite

STEAM

An idea of the importance of steam as a
raw material in the manufacture of blue gas
is given by the proportion of 18 pounds of

steam to 12 pounds of carbon in the blue-gas reaction when carbon monoxide and hydrogen alone are formed. As previously indicated, the amount of steam decomposed is about 25 pounds per 1,000 cubic feet of typical blue gas. In practice 40 to 50 pounds of steam is used per 1,000 cubic feet of blue gas and 30 to 40 pounds per 1,000 cubic feet of carburetted water gas. The discussion of making steam for the blue-gas plant is entirely outside the scope of the present section. It may be mentioned, however, that in a blue-gas plant all the steam needed in the generator may be obtained from the waste-heat boiler of the apparatus, and that in a carburetted-water-gas set 50 percent or more of all the required steam may be made in the waste-heat boiler. It seems desirable also to discuss here the advantages of superheated steam and the use of exhaust steam in the manufacture of blue and carburetted blue gas.

Superheating of Steam in Blue-Gas Manufacture. From the facts that steam is decomposed more rapidly and also the resulting blue gas is of better quality at higher temperatures it might be expected that there would be a very decided advantage in the use of superheated steam in the process. It may be easily calculated that the difference in the heat content of dry steam at 338° F (100 pounds gage pressure) and of superheated steam at 800° F is about 7 percent of the amount of heat absorbed in the decomposition of the steam by carbon to form carbon monoxide and hydrogen. Whether it is more economical to furnish this heat by means of a separately fired superheater or from the fuel in the blue-gas generator is a question that must be settled by balancing the costs of fuel and operation. If exhaust steam which is never dry is used for making blue gas, the advantages of superheating become

more decided. Meade [74] cited a comparison of four 12-foot carburetted-blue-gas machines at Chicago in which the fuel for generators, boilers, and superheaters when superheated exhaust steam was used was 36.76 pounds per 1,000 cubic feet of gas made and 41.93 pounds when live steam was used—a saving of 5.17 pounds of fuel for the superheated exhaust steam. The superheating of the steam in its passage through the superheater and carburetter is no doubt part of the advantage of the back-run process (page 1738), and since this process has been so widely adopted there appears to be little call for other methods of superheating the steam used in the water-gas generator. However, results of recent tests by one of the large United States companies showed no practical advantage in superheated steam in carburetted-water-gas manufacture.

Use of Exhaust Steam in Making Blue Gas. The steam accumulator is a device for storing the steam, which has been used in turbines for driving the air blowers and for other purposes around the water-gas or blue-gas plant, so that it may be used as process steam during the gas-making runs. The accumulator is a well-insulated steel shell generally 6 to 8 feet in diameter by 20 to 30 feet long fitted with an inlet pipe, a steam dome, and an outlet pipe. It is kept about three-quarters full of water and has a submerged perforated pipe which is connected to the inlet pipe and through which the steam escapes into the water. The accumulator works on the principle that, if the exhaust steam under a few pounds of pressure is led into water, as it condenses it heats the water finally up to the temperature of saturated steam at the pressure in question. If the valve on the outlet line is then opened the pressure is

74 See p. 742 of ref. 54.

lowered and some of the water flashes into steam. In this way the steam for driving the blower during the blow may be stored for use in the generator during the run.

Schlegel[75] made a careful analysis of the matter of using exhaust steam in the manufacture of water gas and gave facts and figures to prove that for an 11-foot set making 3,500,000 cubic feet per 24 hours for 300 days per year, with a plant evaporation of 8 pounds of water from and at 212° F per pound of boiler fuel, with a saving of 25 pounds of steam in the accumulator per 1,000 cubic feet and with an investment of $12,000 for the accumulator, piping, and exhaust-steam connections, the savings would yield a net return per year on the investment ranging from 56 percent if boiler fuel cost $5 per ton to 97 percent at $8 per ton. A typical layout and some information on the operation of an accumulator have been presented by Kruger.[76] Further information on the subject has been given by Kruger, by Smoot Engineering Corporation, and by Husted,[76] who stated as a formula in connection with steam accumulators: "Water stores between 2 and 3 Btu per pound of water, per pound of pressure change." Efficiencies of 90 percent and above in the regeneration of steam by accumulators were reported by Kruger. These results have justified the use of steam accumulators and made them standard equipment in water-gas plants.

<center>OXYGEN FOR THE MANUFACTURE OF
BLUE GAS</center>

The application of oxygen or of oxygen-rich mixtures in connection with steam to make gas by a continuous process has been discussed in the producer-gas section (see pages 1629–35). The commercial success of all such processes depends upon a cheap source of oxygen. A process which aimed to produce oxygen cheaply from air was developed by the Jefferies-Norton Corporation of Worcester, Mass., and was described by Frey.[77] It operated on the principle of separating oxygen from nitrogen by the distillation of liquid air. The rectifying still was operated at a pressure of 300 pounds per square inch. The process also made use of expansion engines with fiber-lined cylinders which enabled most of the nitrogen to be brought up to atmospheric temperature in heat exchangers while still under 300 pounds of pressure. This nitrogen was then superheated with oil or gas fuel and used in expansion engines to develop power for the process. The whole system was a reversible cycle with theoretical efficiency of unity. If mechanically perfect, power would be required only to compress the oxygen and nitrogen from their respective partial pressures in air to atmospheric pressure and would amount to about 3 horsepower per 1,000 cubic feet of oxygen. A plant built at Worcester was designed to furnish 100 cubic feet of oxygen per minute at a cost estimated at 50 cents per 1,000. It was calculated that in a plant furnishing 2,000 cubic feet per minute the cost should be 10 cents per 1,000. However, no later record has been found regarding the actual operation of this process.

Knowlton,[78] from experiments with the use of oxygen and steam in a generator with a 25-inch-diameter fuel bed, concluded that to be economical in the manufacture of blue gas oxygen should be produced at

75 Schlegel, C. A., *Proc. New England Assoc. Gas Engrs.*, **1925**, 38–60.

76 Kruger, R. E., *Proc. Am. Gas Assoc.*, **1925**, 1242–3, **1926**, 937–8. Smoot Engineering Corp., *ibid.*, **1926**, 962–3. Husted, W. W., *ibid.*, **1928**, 1332–4.

77 Frey, A. C., *Proc. Am. Gas Assoc.*, **1925**, 1223–32.

78 Knowlton, L. E., *ibid.*, **1929**, 1226–9.

a cost per 1,000 cubic feet not exceeding the cost of 20 pounds of coke. The possibility of producing oxygen and hydrogen for use in gas manufacture by the electrolysis of water with off-peak current from large electric power stations has also been discussed.[79] It is evident, however, that the large-scale use of oxygen in the gasification of coal still awaits a source of cheap oxygen.

COMMERCIAL BLUE-GAS PROCESSES

Data showing operating results of blue-gas apparatus in the United States are rather scarce in the literature. In general it may be said [80] that the generator fuel per 1,000 cubic feet of blue gas will run about 38 pounds of coke or about 40 pounds of good bituminous coal carefully sized (say, 4 to 6 inch) and free from all fines. This is assuming that little blow-run is used so that the heating value of blue gas will be about 300 Btu per cubic foot. The amount of steam used per 1,000 will be about 45 pounds, and the volume of generator air per 1,000 will be almost 1,800 cubic feet.

For best economy the blue-gas apparatus should be operated in connection with a waste-heat boiler. When bituminous coal is used only the blast gases are generally passed through the boiler. The waste-heat boiler will then give an equivalent evaporation of about 50 pounds per 1,000. With coke, if only the blast gases are sent through the boiler, the evaporation will possibly be a little less, but if both the blast and blue gases are passed through the boiler the evaporation will probably be increased to about 70 pounds per 1,000.

The blow-run consists of closing the stack valve at the end of the regular blow immediately after turning off the secondary air blast and continuing the generator blast with the stack valve closed. This forces the producer gas formed during this period through the wash box and into the gas main. By means of more blow-run, which reduces the heating value of the blue gas, and by using the back-run or other combinations in operating, different variations in the above figures may be obtained. The capacity may be varied as much as 20 percent, the generator fuel about 10 percent, and the evaporation in the waste-heat boiler may be reduced as much as 50 percent.

In Tables VI and VII are given data and heat-balance figures based upon average results obtained for the month of January, 1922, in the operation of three 11-foot Western Gas Construction Company's blue-gas sets,[6] and, for comparison, similar data and figures based on results obtained during Test D of the *Tenth Report of the Joint Gas Research Committee*, which may be considered typical of British practice in the manufacture of blue gas.[81]

It is interesting to note from the American results the sources of the heat recovered in the waste-heat boiler, which were as follows:

	BTU
From blue gases	15,400
From undecomposed steam	13,500
From blast gases	37,800
Total	66,700
Less 3 percent estimated loss from blowing down and radiation from boiler Net recovered	64,700

This amount of heat, 64,700 Btu, was 14.1 percent of the heat in the coke or

79 Clark, F. G., *Can. Elec. News.* **28**, 30–3 (1919); *Elec. Engr.*, **50**, No. 3, 197–203 (1931).

80 Battin, W. I., private communication.

81 Parker, A., *Trans. Inst. Gas Engrs.*, **21**, 322–36 (1922–3).

TABLE VI

ACTUAL RESULTS IN THE MANUFACTURE OF BLUE GAS

	Ameri-can [6]	Brit-ish [81]	Ameri-can [82]
Material per 1,000 cu ft			
Coke, dry, lb	34.7	38.8	33.8
Air for blast, cu ft	2,230	1,720	1,610
Steam used, lb	51.9	34.6	49.6
Moisture in coke, lb	1.5	4.7	....
Steam decomposed, lb	23.85	....	....
Steam undecomposed, lb	29.55	....	....
Analysis of coke:			
Moisture, percent	4.20	10.8	....
Volatile matter, percent	2.69	....	0.8
Fixed carbon, percent	89.80	....	92.2
Ash, percent	7.51	12.3	12.3
Heating value, Btu per lb	12,650	11,260	....
Analysis of blue gas:			
Carbon dioxide, percent	5.4	4.5	5.3
Oxygen, percent	0.7	0.1	0.2
Carbon monoxide, percent	37.0	40.7	39.2
Hydrogen, percent	47.3	49.2	48.6
Methane, percent	1.3	0.6	0.8
Nitrogen, percent	8.3	4.9	5.8
Total heating value, Btu per cu ft	287	296	285
Analysis of blast gases entering the waste-heat boiler:			
Carbon dioxide, percent	19.9	....	....
Oxygen, percent	1.1	....	....
Nitrogen, percent	79.0	....	....
Temperature of blue and blast gases:			
Entering the waste-heat boiler	1,300° F	....	1,250–1,300° F
Leaving the waste-heat boiler	550° F	....	400–420° F
Steam from waste-heat boiler:			
Pounds per 1,000 cu ft	57 0	....	33.8

22.5 percent of the heating value of the blue gas made. It is equivalent to the evaporation of 66.7 pounds of water from and at 212° F. With a works evaporation of 8 pounds from and at 212° F, the heat saved in the waste-heat boiler represents a saving of 8.3 pounds of boiler fuel per 1,000 cubic feet of blue gas made. On the other hand, in the British test in which no waste-heat boiler was used, the largest item by far in the heat losses was that of the potential heat of carbon monoxide in the waste blast gas, which amounted to 21.3 percent of the heat in the generator fuel. Also in this test without a waste-heat boiler, the loss due to sensible heat in the blue and blast gases was nearly double that in the American test. These results show what may be expected in the operation of a blue-gas plant and the importance of the waste-heat boiler in the manufacture of blue gas.

BLUE GAS FOR CHEMICAL PROCESSES

On account of its high percentage of hydrogen, blue gas is important as a source of hydrogen for use in chemical syntheses. The hydrogen from blue gas may be used: (1) by itself for a hydrogenating agent as in the hydrogenation of oils; (2) in combination with carbon monoxide for the manufacture of methanol, higher alcohols, or hydrocarbons; (3) in combination with nitrogen for the production of synthetic ammonia.

In any event, the first step is the production of blue gas. This may be done in apparatus already described. However, when the demand for blue gas is very large, of the order of hundreds of millions of cubic feet per day, as in large synthetic chemical plants, the blue-gas generators are much larger than those common in the fuel-gas industry. Developments in large blue-gas plants which are known to be applied in synthetic chemical plants here and abroad have not been published, and the author has failed in his attempts to obtain such information for publication. We can, therefore, only infer what might be the state of the art in this respect.

Rambush [83] in 1931 discussed the design

[82] Young, H. B., *Proc. Am. Gas Assoc.*, 1932, 901–2.

[83] Rambush, N. E., *Proc. 3rd Intern. Conf. Bituminous Coal*, **1**, 840–65 (1931).

TABLE VII

Heat Balance

Calculations based on 1,000 cubic feet of blue gas, 60° F

	American [6]		British [81]	
	Btu	Percent of Heat in Coke	Btu	Percent of Heat in Coke
Heat in				
Item 1. In coke burned	458,040	100.0	490,000	100.0
2. In steam used	58,932	12.8	38,600	7.9
3. In blast	. . . . .	. . . .	. . . . .	. . . .
Total	516,972	112.8	528,600	107.9
Heat out—Recovered				
4. Calorific value in gas	287,000	62.7	296,000	60.5
5. Steam made in waste heat boiler				
(a) 51.9 pounds used under grate 58,932				
(b) Heat in excess steam 5,768				
Total	64,700	14.1	. . . .	. . . .
Heat losses				
6. Sensible heat in blue gas and blast gas to condenser and stack	31,130	6.8	63,300	12.8
6a. Potential heat in blast gas to stack	. . . . .	. . . .	104,200	21.3
7. Sensible heat in undecomposed steam and moisture from coke to condenser	6,970	1.5		
8. Latent heat lost in undecomposed steam and coke moisture	29,550	6.4	16,300	3 3
9. Loss in unburned carbon in ashes	59,000	12.9	29,400	6.0
10. Radiation, boiler blowdown, and all other losses	38,622	8.4	19,400	4.0
Total	516,972	112.8	528,600	107.9

of large water-gas generators as built by Power-Gas Corporation, Ltd., and installed at the works of Synthetic Ammonia and Nitrates, Ltd., at Billingham, England. He brought out the following points:

1. Blue-gas generators were built with internal diameters up to 15 feet and with capacities up to 10 million cubic feet per day. They were believed at that time to be the largest blue-gas generators in the world. These large generators were required to be of the mechanical type in which the principles of construction fol-

lowed the design developed previously in connection with mechanical gas producers.

2. In order to minimize fluctuations in blue-gas composition and eliminate variations in operating procedure, the fuel had to be introduced mechanically in small increments.

3. For high rates of gasification, the refractory generator lining was replaced by water in jacketed steel as previously proved desirable in producer-gas practice. In the discussion, it was brought out that the necessity for vertical depth of the water

jacket depended upon the ash-fusion characteristics of the fuel. High capacity was possible with some fuels without the water jacket.

4. A dry seal in the base of the generator was necessary, since large blue-gas generators were operated with blast pressures up to 100 inches water gage. The grate design was usually the result of some 30 years of previous experience in gas producers and seemed unlikely to be capable of modification by more than minor improvements.

5. The valves in operation should be automatically timed and mechanically controlled.

6. For efficient operation, the potential and sensible heat in the blow gases and the sensible heat in the blue gas must be recovered. This could be done by means of waste-heat boilers or preheaters for the steam used in the process.

7. When the blue gas was to be utilized in the manufacture of ammonia, the operation could be modified by the introduction of steam and air to produce continuously a semi-water gas of which a typical composition was carbon dioxide 5.0, carbon monoxide 35.0, hydrogen 38.0, methane 0.5, and nitrogen 21.5 percent.*

Excepting such differences as may be produced by the increase in the size of the generator, points upon which no information is at present available, items 2 to 6, inclusive, have been covered in the discussion of the manufacture of blue gas and carburetted blue gas for fuel purposes.

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* It appears doubtful that gas of this composition could be made continuously by passing air and steam through a hot fuel bed, for the heat absorbed in making the blue gas is nearly twice that which could be furnished in making the producer gas calculated from the nitrogen content. Gas of this composition might be made continuously by using an oxygen-enriched mixture and scrubbing out part of the carbon dioxide formed.

Continuous operation for the production of semi-water gas is a modification of the producer-gas process which has also been discussed in another section (see pages 1629–35), and reference will be made to it later. With regard to possible increase in size beyond 15 feet internal diameter of the generator, Rambush [83] believed that, if the demand justified a capacity of 20 or even 30 million cubic feet per day per generator, there should be no serious difficulty to overcome in the design, construction, or operation of such larger units.

In the production of hydrogen from blue gas special methods of purification are necessary. Tar and hydrogen sulfide are removed by methods common to the gas industry. If the maximum total sulfur allowable is of the order of 0.1 grain per 100 cubic feet,[84] special processes for the removal of organic sulfur are necessary.[85] (See pages 1815–7.) Iron carbonyl is a poison to the catalyst used in the methanol synthesis and may be removed by passing through activated carbon. Carbon dioxide in small amounts may be removed by scrubbing with water solutions of ethanolamines [86] or of diaminoisopropanol.[87] When necessary, carbon monoxide may be removed by catalytically oxidizing with steam to carbon dioxide and scrubbing out the bulk of the carbon dioxide with water under pressure.[88] This increases the yield of hydrogen. Hydrogen may also be separated from carbon monoxide by liquefaction.[89] When the hydrogen is to be used

[84] Underwood, A. J. V., *Ind. Eng. Chem.*, **32**, 449–54 (1940).

[85] Fischer, F., *J. Inst. Fuel,* **10**, 10–4 (1936). Wilke, G., *Chem. Fabrik.*, **11**, 563–8 (1938).

[86] Hirst, L. L., and Pinkel, I. I., *Ind. Eng. Chem.*, **28**, 1313–5 (1936).

[87] Gregory, L. B., and Scharman, W. G., *ibid.*, **29**, 514–9 (1937).

[88] Anon., *ibid.*, **22**, 433–7 (1930).

[89] Pallemaerts, F. A. F., *ibid.*, **21**, 22–29 (1929).

with nitrogen for the manufacture of synthetic ammonia, the carbon monoxide may be catalytically oxidized to carbon dioxide with air, which also introduces the necessary nitrogen into the mixture.

The cost of hydrogen made from blue gas varies according to the size, location, and other conditions surrounding the plant. Cost figures for large plants are not available, but it is known that blue gas represents one of the cheapest sources of hydrogen for large-scale chemical manufacture.[90]

CARBURETTED BLUE OR WATER GAS

Reference has already been made to the fact that attempts to enrich blue gas were not successful until the invention in 1872–5 by Prof. T. S. C. Lowe at Norristown, Pa., of a system which used, for making the enriching oil gas, a separate chamber that was heated internally by combustion of the producer gas formed in the generator during the blow. Later, aided by cheap naphtha and gas oil—byproducts in the production of lamp oils and lubricating oils from petroleum—there was a period of rapid development in the size and form of the apparatus, and by 1882 a considerable percentage of the manufactured-gas output in this country was carburetted blue gas.[91] In the development during this period of the original Lowe apparatus into the three-shell form used today by United Gas Improvement Company of Philadelphia, their general superintendent, Dr. Alexander C. Humphreys, had a leading part. As shown in Table VIII, the production of carburetted blue gas reached a peak in 1926, when it represented nearly 60 percent of the total manufactured gas in the United States. Since that time on account of the

spread of natural gas supplied by long transmission pipe lines and the installation of more byproduct coke ovens by gas companies, both the volume of carburetted blue gas produced and the percentage of carburetted blue gas in the total manufactured gas have declined.

Carburetted-Blue-Gas Plant. As was shown in Fig. 2, the carburetted-blue-gas apparatus consists of three brick-lined cylindrical steel vessels—the generator, the carburetter, and the superheater. The generator with its blast connection, its top and bottom steam inlets, its fuel bed, and its bottom and top gas offtake pipes has been discussed earlier in this chapter. The carburetter and superheater are connected at

TABLE VIII

Manufactured Gas Produced and Purchased for Distribution to Consumers in the United States [92]

	Carbu- retted Blue Gas Produced	Coal and Coke-Oven Gas		Oil Gas Pro- duced	Total Manu- factured Gas	Percent of Carbu- retted Blue Gas
		Pro- duced	Pur- chased			
			billions of cubic feet			
1919	180	65	29	26	300	60
1922	222	54	53	25	354	63
1926	252	71	84	31	438	58
1929	224	95	118	34 *	471	48
1933	144	77	76	13 *	310	46
1936	148	78	85	16 *	327	45
1939	157	70	87	22 *	336	47

* Includes refinery oil gas, reformed refinery oil gas, reformed natural gas, and butane-air gas.

the bottom by a brick-lined gasway and are partly filled with checkerbrick. At the top the carburetter is connected to the gas offtake from the generator, and provision is made for introduction of secondary air and of the enriching oil. At the top of the superheater there are a stack valve and a gas connection leading to the wash box. Other types of water-gas apparatus

90 Groggins, P. H., *Unit Processes in Organic Synthesis,* McGraw-Hill Book Co., New York, 1938, pp. 422–9.

91 Stone, T. W., *Proc. Canadian Gas Assoc.,* 1926, 185–215.

92 Ryan, P., *Am. Gas Assoc., Statistical Bull.* 8 (1930), 31 pp., 44 (1941), 25 pp.

have been used, and certain important modifications have been made in this type. It will be simpler, however, to consider this three-shell set, which was developed by the United Gas Improvement Company and is now made by other builders also, as standard apparatus.

Outline of Carburetted-Water-Gas Process. In this process, just as in the blue-gas process, the apparatus is heated by alternate blows, and gas is made by alternate runs. During the *blow*, a producer gas high in carbon dioxide is formed in the generator and is burned by secondary air admitted at the top of the carburetter. The hot products of combustion traveling down through the checkerbrick of the carburetter and up through the superheater heat these parts of the apparatus and then pass on through a waste-heat boiler or directly from the top of the superheater to the stack. During the *run*, blue gas is made in the generator and oil is sprayed into the top of the carburetter. The mixture of blue gas and oil vapors passes down through the checkerbrick of the carburetter and up through the superheater. In their passage through the hot checkerbrick, the oil vapors are cracked to permanent gases. The mixture of blue gas and oil gas is the carburetted blue gas which passes from the top of the superheater through the wash box and hot main to the purifying apparatus. Since the gas-making process is an intermittent one a small relief holder is provided so that the flow of gas through the main part of the purifying apparatus may be constant. Reference to the flow diagram in Fig. 8 should give a clear idea of the general process.

Essentially the manufacture of carburetted blue gas is a combination of the manufacture of blue gas and of oil gas accomplished simultaneously in connected pieces of apparatus. The manufacture of blue gas has already been treated.

Carburetter and Superheater Construction. As illustrated in Figs. 2 and 9, the carburetter and superheater are firebrick-lined steel shells of practically the same diameter as the generator. The carburet-
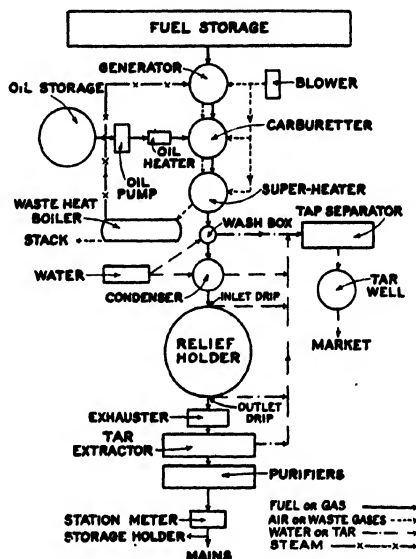
Fig. 8.   Material flow sheet for carburetted-blue-gas plant.

ter also has about the same height as the generator, but the superheater is 8 to 10 feet taller. The foundations for the carburetter and superheater are of concrete or masonry, but, to prevent overheating, the bottom plates are sometimes supported on I-beams which are spaced a few inches apart and rest on the foundations.

The linings of the carburetter and superheater consist of 1 or 2 inches of insulation and 9 to 12 inches of fireclay which may be made of one layer of thick blocks or two layers of circle brick. At the top, the carburetter and superheater may be dome
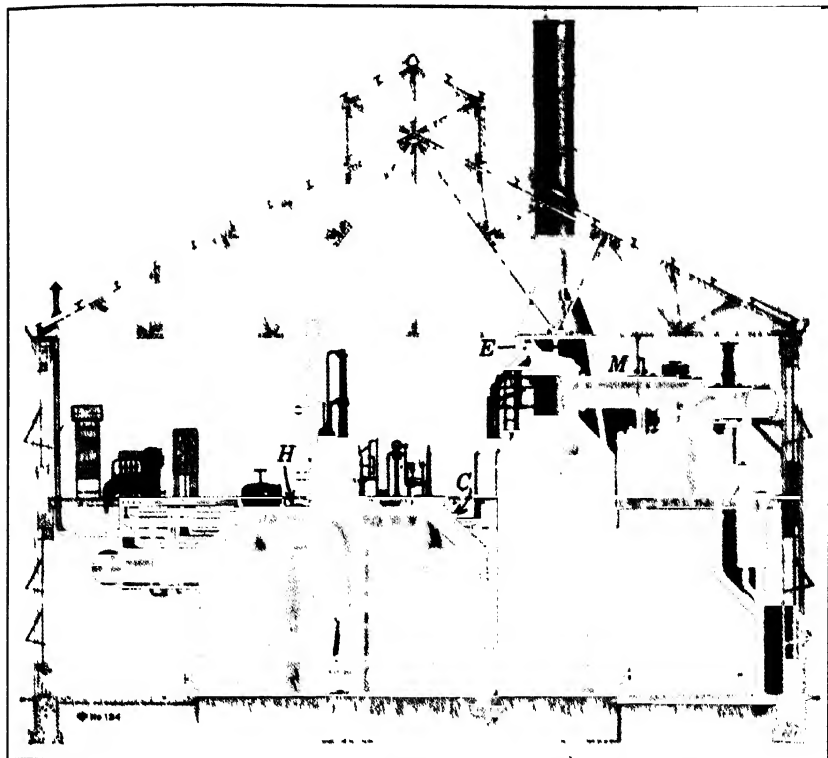
FIG 9   Standard U G I cone top carburetted blue gas apparatus

shaped or cone shaped or flat If they are
flat the interior of the lining is made more
or less cone or dome shaped by corbeling
the blocks or brick in towards the center

The carburetter and superheater are
connected at the bottom by a firebrick-
lined passage or gasway, and each contains
at its bottom heavy fireclay arches upon
which are supported rows of heavy blocks
of tile This arrangement is illustrated in
Fig 2. The checkerbrick, with which both
chambers may be filled for a greater por-
tion of their height, rest upon these tile
blocks, which are usually 10 inches deep

by 5 inches wide and spaced 4 inches
apart   The checkerbrick are commonly
9 by 4 5 by 2 5 inches, and their arrange-
ment varies   The first course at the bot-
tom is laid by placing the brick on edge
end to end without mortar in parallel
rows which are spaced evenly   The second
course is then laid with the rows perpen-
dicular to those in the first course   In
laying the third course the rows may be
placed so that the brick in course three
come directly over the spaces in course one
This gives the staggered arrangement
shown in the carburetter in Fig. 2. If the

spaces in course three are over the spaces in course one it gives the flue arrangement shown in the superheater of Fig. 2.

The function of the checkerbrick during the runs is to gasify the oil with heat which is absorbed from the blast gases during the blows. The efficiency in the performance of this function depends principally upon the amount of checkerbrick, their arrangement, and spacing. It would lead too far to attempt here to go into the details which are discussed elsewhere.[93] When heavy oils which leave large amounts of carbon residues are gasified the checkerbrick of the carburetter may be omitted in whole or in part.

At the top of the carburetter, provision is made for introducing the secondary air, called carburetter blast, whose function is to burn the carbon monoxide in the blast gases and thus make the heat of combustion, as well as the sensible heat, available for heating the checkerbrick. The method of introducing this secondary air has been investigated by Schaaf,[94] who advocated the introduction of the secondary air through nozzles distributed around the circumference of the large gas connection between the generator and carburetter. Sometimes only part of the carbon monoxide in the blast gases is burned by the secondary air, and provision is made for the addition of tertiary air at the bottom of the superheater.

Since carbon formed in the cracking of the oil and dust from the blast products are deposited on the checkerbrick it is necessary from time to time to shut down and remove and clean the checkerbrick in the set. The length of time in ordinary operation the sets may be run before it is necessary to rechecker the carburetter

varies from 500 to 2,800 hours,[95] and the time between recheckering of the superheaters from 1,100 to 19,000 hours. In place of brick it has been proposed to use special fireclay tile,[96] and the use of castings of heat-resisting alloys at the top of the carburetter where the wear is most severe has also been investigated.[97] In carburetting with heavy oils, use may be made of checkerless carburetters,[98] to which reference has already been made.

The oil for enriching the blue gas is mainly introduced through an oil spray into the top of the carburetter. Since this oil represents 40 to 60 percent of the cost for materials in the manufacture of blue gas the importance of the oil spray is evident. In earlier practice the oil sprays were of solid stream type from which the oil was forced under a pressure of 15 to 30 pounds per square inch in a number of fine streams. Later the atomizing or mist type of spray became common. In this type the oil is delivered to the spray at higher pressures up to 250 pounds per square inch. The spray in either case should deliver the oil evenly over the full area of the top of the carburetter checkerbrick. To protect it, the oil spray is arranged so that it can be withdrawn into a recess at the top of the carburetter during the blow periods, or it may be water cooled. For purging the oil out of the line beyond the operating valve and steaming out the spray at the end of each run, a steam connection is made to the oil line. The oil line is also provided with an oil meter, of which the indicator is located on

[93] See pp. 490–7 of ref. 7.

[94] Schaaf, A. H., *Gas Age-Record*, 64, 145–8 (1929).

[95] Wolfe, J. H., *Proc. Am. Gas Assoc.*, 1925, 1244–59.

[96] Eck, L. J., and Wolfe, J. H., *Joint Proc. Conf. Am. Gas Assoc.*, 1931.

[97] Parmelee, C. W., Westman, A. E. R., and Pfeiffer, W. H., *Univ. Illinois Eng. Exp. Sta., Bull.* 179 (1928), pp. 1–88.

[98] Wolfe, J. H., *Proc. Am. Gas Assoc.*, 1924, 809–12.

or near the instrument board. When heavy oils are used, provision must also be made for an oil heater in the line.

At the top of the superheater is located the stack valve through which the blast products may be vented during the blows. Here also provision is made for connections

Automatic Controls. Reference has already been made to automatic controls for blue-gas apparatus. Their use in the carburetted-blue-gas process is equally important and has been well discussed elsewhere.[99] In large plants, the size of the hot main by which the gas is led from the
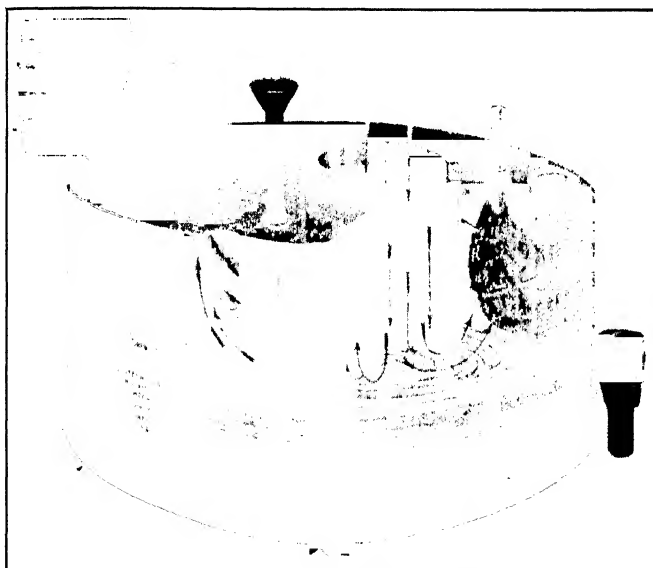
FIG. 10. Western seal tar batter, a form of wash box.

to the waste-heat boiler and to the gas offtake which leads to the wash box. The function of the wash box is the same as has been described for the blue-gas generator except that provision must be made in the wash box of the carburetted-blue-gas set to take care of considerable amounts of tar from which straight blue gas is almost free. One form of wash box is known as the seal tar batter, in which as illustrated in Fig. 10 there is a special arrangement of baffles and water spray to remove the tar from the gas more thoroughly than when it is simply bubbled through water.

generator house, the steam and blower capacities, and the practice of using one waste-heat boiler for two sets make it desirable that a certain sequence of operation be maintained among the different sets with relation to each other. This may be accomplished automatically by means of a synchronizer [100] or master control device [101] which is designed to control the automatic

99 Stevick, C H., *Am Gas Assoc. Monthly*, **5,** 107–27 (1923).

100 Merritt, M. H., *Proc. Am. Gas Assoc.*, **1928,** 1365–9.

101 Gas Machinery Co., *Gas Age-Record*, **63,** 221 (1929).

devices operating the individual sets in such manner that they are kept in definite relation to each other.

Regular Operation of a Carburetted-Blue-Gas Apparatus. The regular operation of this apparatus has been discussed at considerable length elsewhere,[102] and full directions are always furnished by the builders of the apparatus. Hence only an outline of important points will be given here. The operation of the generator itself is the same as previously described for the blue-gas process.

The method of drying out the carburetter and superheater and of igniting the blast gases for heating the checkerbrick has been described in connection with the igniter of the blue-gas apparatus. In the manufacture of carburetted blue gas, however, the subsequent blasting is regulated not only to bring the generator fire up to gas-making temperature but also to heat the checkerbrick of the carburetter and superheater to the temperature best suited for the gasification of the enriching oil. Hence, after the carburetter is lighted and the carburetter blast valve adjusted so that the brightest and most uniform flame is produced in the carburetter, the blasting is continued in this manner only until the top checkerbrick of the carburetter become red. At this point the carburetter blast valve is raised further to add an excess of air in order to carry the heat through the checkerbrick of the carburetter and superheater and also to prevent overheating the top of the carburetter. The first blow on a new machine or on one that has been idle for some time will require from 10 to 20 minutes, varying with the fuel and other conditions. It is continued in the way described until the top of the fire as seen through the sight

cock at the top of the generator is dull red, the brick in the top of the carburetter are bright red, and those in the bottom of the carburetter show a faint color, at which point the apparatus is ready for the first run. This run is made in the same way as a regular run, which will be described later, except that no oil is used unless absolutely necessary in order to prevent decreasing too much the heating value of the gas in the holder. The use of oil in the first runs delays the heating of the checkerbrick.

Just previous to making the first run, the valve on the gas outlet of the wash box is cautiously opened, care being taken that all the valves between there and the relief holder are open and that none of the drips contain enough liquid to seal the line. These first runs without oil should be short up-runs. They serve the double purpose of avoiding overheating the grate bars and of preventing the temperature in the top of the carburetter from becoming too high, both of which conditions might result from too long a blow. During these runs the temperature in the superheater will be raised considerably by the heat carried over in the hot blue gas. In one test which came to the author's notice, after the generator had been heated with a slow fire under natural draft for 30 hours, the first blow of 15 minutes raised the temperature at the bottom of the superheater from 320° to 1,200° F, and five more blows alternating with short runs were required to bring the temperature at this point up to the operating temperature of 1,500° F. In the same test it required 75 minutes to bring the temperature of the top of the superheater from 280° to 1,000° F, and nearly another hour to bring the temperature at this point to an even operating temperature of 1,080° to 1,160° F.

After the apparatus has been heated and the fuel bed is in condition for making gas the problem remains of fixing the proper cycle and balancing the set. In the discussion on blue gas this question was considered as far as it related to the generator fire. Here, however, it is necessary also to take into account the maintenance of temperatures in the carburetter and superheater which will give the most efficient gasification of the oil. This will be kept in mind in the following treatment, and balancing of the set therefore will consist mainly in determining the proper steam input to the generator to give the highest all-around efficiency of operation with a given fuel and a given blast pressure.[103]

The length of blow must be assumed; it will vary from 2 to 4 minutes. Shorter blows involve too much work with hand operation and consume too great a proportion of time in changing valves. The upper limit is possible only with a dense fuel. The volume of air entering the generator should be measured. Experience has shown that for 525-Btu gas the percentage of the total blast entering the generator will be about 75 and that from 1,400 to 1,700 cubic feet of generator air is required per 1,000 cubic feet of gas made. For efficient operation and high capacity, the blast should be at the rate of not less than 100 cubic feet per square foot of grate area. Provision for 150 cubic feet of generator air per square foot of grate area is often made. Light porous cokes require more air than dense anthracite coals.

If the amount of air passing through the generator on the blow is known, the amount of gas to be made during the run may then be calculated. The theoretical amount of steam necessary to generate

[103] Knowlton, L. E., private communication.

1,000 cubic feet of carburetted water gas when using 4 gallons of oil is about 17 pounds. In practice it takes from 27 to 35 pounds according to the fuel, being lowest with anthracite and highest with light cokes. When about 2.7 gallons of oil per 1,000 is used, giving a 525-Btu gas, the theoretical amount of steam is approximately 19 pounds, and in practice 30 to 40 is required. With a short blow the amount of heat to be taken out on the run is comparatively small. The run may then be short without an excessive rate of steam. If the run is made long and the steam rate reduced, the capacity of the set will fall off with increase in labor cost. In general, with hand-operated sets, the total length of cycle cannot be less than 5 or 6 minutes without rendering the gasmaker's work excessive. The length of run would then be 3 to 4 minutes. After the length of run and the quantity of steam to be admitted have been determined, the rate of admission may be calculated. This rate may be best maintained by means of steam flow meters.

With automatic operation it is possible to shorten the cycle and increase efficiency by maintaining a more even temperature in the generator and thus approach the ideal condition of continuous gas-making. For this reason, the shorter cycles tend to decrease the fuel and steam required per 1,000 but reduce capacity when shortened below a certain limit by reason of high proportion of time lost in valve changes.

The modern practice in admitting steam is to divide each run into up- and down-steam periods. The run may start with either up- or down-steam but must end with a sufficient up-steam period to purge all blue gas from the base of the generator before the entrance of the blast. The allowable percentage of down-steam will vary with characteristics of different fuels

from 45 to 55 percent of the total steam admitted.

Starting as outlined above with an assumed length of blow and a rate of blasting fixed by local conditions, an excess of carbon monoxide which cannot be utilized in the carburetter may be formed at the end of the blow. There are several ways of overcoming this. If the fire cleans easily and there is no excessive or hard clinker on the grates, the percentage of down-run can be increased. As the air passes through the fire the oxygen reacts with the fuel and forms carbon dioxide, which is reduced to carbon monoxide as it passes through the hot carbon in the upper part of the fire. The hotter the fire, the greater the amount of this reaction. Also, the slower the rate at which the carbon dioxide passes through, the more time allowed for the action of the hot carbon, and consequently the greater this reaction. The increase in down-run, cooling the top of the fire, reduces the amount of this reaction and overcomes the waste of carbon monoxide at the end of the blow. The increase in down-run will tend to harden the clinker on the grate, and, if the clinker is already as hard as can be conveniently handled, the down-run should not be increased. Instead a somewhat shallower fire may be tried, provided that the carbon dioxide in the finished gas is not excessive. This will give a smaller zone to react on the carbon dioxide in the blast gases. The carbon dioxide in the finished gas will range from 3.5 percent to 5.5 percent, according to the fuel, being lowest with dense and highest with light fuels. If the carbon dioxide in the finished gas is high, the only remaining method of overcoming a waste of carbon monoxide during the blow is to shorten the blow or, if possible, increase the rate of blasting. This necessitates shortening the run, unless the cycle is already at the minimum, in which event the rate of steam input will have to be decreased proportionally.

Since the percentage of carbon monoxide in the blast gases coming from the generator is low at the beginning and increases as the blow proceeds, provision should be made to increase the amount of secondary air supplied by the carburetter blast as the blow continues. Whether tertiary air is supplied by a superheater blast is a matter of choice, but many operators prefer to add enough air to complete the combustion of the carbon monoxide in the blast gases at the top of the carburetter and depend upon the heat to the superheater being supplied by the sensible heat in the blast products.

All sets should be equipped with a pilot light, which is a small gas flame so adjusted that it will impinge on the blast products issuing from the superheater to the stack. If more than 2 percent of carbon monoxide is present it will ignite and burn with a blue flame. This enables the gasmaker to regulate the amount of secondary air (and tertiary if used) so that there is less than 2 percent of carbon monoxide in the stack gases.

The Orsat gas-analysis apparatus is a valuable aid in operation, for it enables one to tell not only the percentages of carbon dioxide, carbon monoxide, and oxygen in the blast gases at various points in the apparatus but also the percentage of carbon dioxide in the carburetted blue gas. As has been pointed out in the operation of the blue-gas apparatus, the percentage of carbon dioxide in the gas is a direct and reliable indication of the efficiency of the steam decomposition and of the condition of the generator fire. Carbon dioxide in the carburetter blue gas in excess of 4 to 5 percent is caused by too great an excess of undecomposed steam, which results from

too cool a fire or poor conditions in the fire, that is, weak spots or blow holes through which much of the steam passes without being decomposed. Reference was made in the blue-gas process to the use of steam-decomposition meters which are also important in the carburetted-blue-gas process. In addition to such indications on the composition of the gas as may be obtained in the generator house, regular complete analyses and heating-value determinations should be made on the purified gas at the station meter. The results of these will be helpful not only in the calculation of oil efficiencies but also in giving the average percentage of carbon dioxide.

The operation during the blow may easily be inferred from the above discussion. To change from blow to run, the carburetter blast valve (or the superheater blast valve) is closed exactly on time and followed quickly with the closing of the generator blast valve. If the set has an individual blower, the steam to the turbine is turned off at this point. The valve admitting steam to the generator is next opened, the stack valve closed, and the pressure gages observed to make sure that they are registering and that no back-pressure is building up.

The valves on the oil line are now opened, starting with that next to the spray and regulating the flow of oil by the valve at the inlet to the oil meter so that the desired quantity will be admitted ¾ to 1½ minutes before the end of the run. On the first runs after starting up or after coaling, the amount of oil should be considerably less than the regular quantity; in the first run of a set which has just been brought up to heat, about one-fourth of the regular amount of oil is used, the amount being gradually increased on each run as the temperatures in the carburetter and superheater increase until the normal

amount is added, say, on the sixth run. As soon as the required quantity of oil has been added, the oil is shut off and all oil between the oil valve and the spray immediately purged from the line by steam which is allowed to flow for about 10 seconds.

If part of the run is to be down-run, the hot valves and steam may be reversed at the desired time without reference to the oil flow provided that the blue gas from the down-run is also passed through the carburetter and superheater. The run may be started either up or down and, as stated under blue gas, may be divided into varying proportions of up-run and down-run, but a few seconds at the end must always be up-run in order to purge the blue gas from the space under the grate and prevent an explosion when the blast is turned on.

To terminate the run and put on a blow if the set has an individual blower, the steam to the turbine is first turned on and then the base steam is shut off exactly on time. The generator blast valve may then be opened and followed in 5 or 10 seconds by the opening of the stack valve. This gives a blow-purge which drives the gas from the apparatus through the wash box. If the opening of the stack valve is too long delayed, the blast products entering the wash box increase the percentage of inerts in the gas. On the other hand, if the stack valve is opened before the generator blast is turned on, as is the practice of some operators, the gas in the set is purged to the stack and wasted.

From 5 to 30 seconds after the opening of the generator blast valve, depending upon fire conditions and never in any event until after the stack valve is opened, the carburetter blast valve is opened part way and then the opening gradually increased as the blow progresses, always fur-

nishing just enough secondary air to prevent a blue flame from appearing at the stack valve. As has been noted, in many of the larger sets this increase in opening of the carburetter blast valve has been made automatic.

If the set is provided with a waste-heat boiler, through which only the blast gases are passed, the change from run to blow is made as described, and after the carburetter blast valve is opened the boiler valve may be opened and the stack valve closed. This sends the blast gases through the boiler. Then the stack valve is opened and the boiler valve closed in the order given just before the termination of the blow.

If the superheater blast is used, it may be turned on right after the carburetter blast. It is regulated in conjunction with the carburetter blast so that no carbon monoxide flame shows at the stack valve. The proportions of carburetter and superheater blast must be regulated according to the temperatures shown by pyrometers in these pieces of apparatus.

We have already noted the modern tendency toward high blast pressures. The actual pressure at the blower outlet varies under different conditions and may be 15 to 40 inches of water pressure. This pressure decreases throughout the set and at the superheater or waste-boiler outlet is reduced to atmospheric pressure. The loss of pressure in the fire and through the checkerbrick is doing useful work; the other losses, although unavoidable, are wasted. If these losses can be reduced, it follows that more air will pass through the set. Also this wasted energy consumes boiler fuel. Where the pressure drop exceeds the following, it would be well to consider enlarging the connections: blower to base of generator, 10 percent; top of generator to top of carburetter, 10 percent;

bottom of carburetter to bottom of superheater, 4 percent; and top of superheater to outlet, 7 percent.

Operating Factors Affecting Oil Efficiencies. The effect of fire conditions on the quality of blue gas has been fully discussed. These conditions have also a very important bearing on oil results for they directly affect the quality of the blast gases, which are used to heat the carburetter and superheater, and thus the temperatures in these chambers. The temperature necessary in the top of the superheater ranges from 1,200 and 1,400° F for different oils, this temperature being usually measured with a thermoelectric pyrometer. The temperature in the carburetter is considerably higher and is seldom measured. Practice has shown that, with proper fire conditions and proper amount of secondary air, the temperature in the superheater is an indication of the temperature in the carburetter.

By observing the overflow water from the wash box, it can be readily seen if the set is making lampblack, or if oil is condensing out. Both these substances float on the water. Lampblack indicates too high temperatures, and oil too low. Between these limits the overflow water is mixed with a dark brown tar. The stain method of determining whether the temperature in the checkerbrick is proper consists in allowing the gas from a small cock at the outlet of the wash box to impinge on a strip of unglazed white paper. Undecomposed oil showing too low a temperature is recognized by an oily transparent stain on the paper. If the temperature is too high, the stain will be black from free carbon. The proper intermediate temperature is recognized by a dry brown stain free from oil. There is a small range of temperature at which the highest efficiency for any given oil is obtained. As there are

no standard specifications for gas oils, the only way to determine this range is by varying temperatures slightly and observing the results. It is, of course, important that the oil be sprayed uniformly over the carburetter. Extremely poor distribution by the spray has been reported [104] to have allowed the oil to cool a channel in the checkering to such an extent that part of it escaped uncracked even when the temperature of the rest of the checkerbrick was raised to the point where lampblack also appeared in the gas. Trouble is often experienced with the temperature in the top of the superheater being too high. Some operators believe that the temperature should be from 50 to 100° lower at the top than at the base of the superheater and should never be higher. An excess of secondary air will tend to raise the temperature in the top of the superheater and under extreme conditions steam may be injected about the middle of the superheater to cool the top.

The rate at which the oil gas passes through the fixing vessels has a remarkable effect on the efficiencies. There have been instances where varying the temperatures from the point where oil was noticed on the overflow of the wash box to the point where lampblack was made, did not give good efficiency. The time for admitting the oil was decreased from 3 to 2 minutes, and immediately the results changed from decidedly poor to very good. Other oils require a slow rate. The importance and effect of the amount and arrangement of the checkerbrick and the questions of temperature control in the oil gasifying part of the apparatus have been discussed by Chairman Wolfe of an American Gas Association Committee, to whose report reference may be made.[95]

104 Ferguson, H. E., private communication, 1929.

SPECIAL OPERATING CONDITIONS AND METHODS

The operating procedures which have been described above as the regular methods of operation are those which best exemplify the fundamental principles of the process and at one time were used almost exclusively. However, a number of other methods of operation now in common use will be discussed as special or modified procedures. These include the use of bituminous coal for generator fuel, the use of heavy oils and cold carburetting materials as enriching agents, the back-run and the reversed air-blast methods of operation, the ignition arch carburetter, the reverse-flow water-gas machine, and the production of low-specific-gravity and of high-heating-value gases in water-gas apparatus.

Bituminous Coal as Water-Gas Fuel. The advantages and disadvantages of bituminous coal for the blue-gas process have already been given. As far as the generator is concerned, the operation of the pier process applies equally here. Major difficulties which apply particularly to the carburetted-blue-gas process are those resulting from the stopping-up of the checkerbrick in the carburetter and smoke in the blast products.

The troubles caused by clogging the checkerbrick in the carburetter with fine fuel blown over from the generator have been remedied partly by means of more efficient dust separators such as the cyclonic dust catcher [1] between the generator and carburetter and partly by wider spacing and flue arrangement of the checkers in the carburetter, or by the use of checkerless carburetters. These allow whatever dust reaches the carburetter to collect at the bottom where it interferes least with the operation and whence it can easily be removed.

The smoke which may escape from the stack in operation with bituminous coal is caused by the tarry matter which is distilled from the raw coal on the top of the fire and carried along in the blast gases. During the part of the blow when the carburetter blast is on, especially if a small excess of secondary air is used, this tarry matter is burned in the carburetter and gives no trouble. However, when operating with bituminous coal this tarry matter and coal gas and the higher percentage of carbon monoxide which results from a lower blast pressure all combine to give the generator blast gases a higher heating value than in operation with anthracite or coke. If these richer blast gases are completely burned the checkerbrick in the superheater will be overheated by the time the generator fire has been brought up to optimum temperature. To prevent this overheating in the superheater, the practice was adopted of closing the carburetter blast valve and continuing the blow with only generator blast until the fire reached the proper temperature. This led to smoke trouble from the tarry matter which escaped unconsumed in the blast gases from the stack.

This smoke trouble is overcome by the back-run and reversed-air-blast processes which will be described later and which were in fact invented for the purpose of preventing smoke in the use of high-volatile western coals. In the regular method of operation this smoke is eliminated by the blow-run,[105] which also finds use in increasing the gas yield in operation with coke.

The blow-run, as the name implies, consists in making a portion of the gas with air instead of with steam. Its application in the prevention of smoke formation and

of overheating of the superheater in operating with bituminous coal is extremely simple. Shortly before the end of the regular blow the carburetter blast is turned off, and immediately thereafter the stack valve is closed. This forces the blast gases into the wash box and adds these blow-run gases to the gas collected in the relief holder. The blow may then be continued until the generator fuel is brought up to gas-making temperature. By a suitable ratio of blow-run to regular blow time the temperatures of the fuel bed and of the checkerbrick may both be brought to the optimum points. The blow-run gas is high in nitrogen and contains considerable carbon dioxide. However, since it is made near the end of the blow it also is high in carbon monoxide and contains some coal gas distilled from the raw coal on the top of the fuel bed which serves to increase the heating value. The tarry matter which causes smoke if the blast products are vented to the stack gives no trouble when they are passed to the wash box and is removed in the regular purification of the gases. Since the time of the blow-run is taken from the blowing period there is no loss in the blue gas made so that the blow-run gas represents a net gain in capacity. The use of the blow-run may require an additional amount of enriching oil, but this amount is slight unless, as will be explained later, a large proportion of blow-run is purposely employed. If the total blowing period with bituminous coal is 3 minutes, the length of the blow-run might be 15 seconds.

The blow-run increases the fraction of the coal gas which is recovered in the use of bituminous coal as generator fuel. Murdock [106] found that the coal gas appeared to be evolved at a constant rate during the cycles. He estimated that, in his ex-

105 Seeley, H. K., *Proc. Am. Gas Assoc.*, **1924**, 777–84.

106 Murdock, W. J., *ibid.*, **1926**, 927–32.

periments on a 12-foot machine, 58 percent of the available coal gas was saved, 50 percent in the runs and 8 percent in the blow-runs, and that coal gas contributed more than 8 percent of the heating value in the finished gas.

The use of steam along with air to the generator in the blow-run has been investigated by Willien,[107] who found that, in a 6-foot water-gas set, using steam during the blow-run at about half the rate of the regular run raised the heating value of the blow-run gases from 102 to 187 Btu per cubic foot and reduced the percentage of nitrogen from 66.4 to 41.5.

Carburetting with Heavy Oils. The gas oil fraction which in the distillation of crude petroleum comes off at a higher temperature than kerosene was formerly the carburetting material universally used in the water-gas process. This fraction, which is made up of hydrocarbons averaging 16 to 20 carbon atoms per molecule and containing considerable percentages of paraffin hydrocarbons, is not only the best carburetting material for the water-gas process but also the most desirable cracking stock for making motor fuel in the oil-refining industry. Hence, with the rapid increase in the demand for gasoline during and after the first World War, the rise in the price of gas oil made it desirable to find a cheaper carburetting material.

Work on the use of heavy fuel oils in the manufacture of carburetted blue gas was started by the United Gas Improvement Company and associated companies in 1920 [108] and resulted in two successful processes.[109] By 1930, one large eastern plant was using a million barrels of heavy fuel oil per year and these processes were being adopted rapidly on the Atlantic seaboard, where large quantities of heavy fuel oils were available at prices fixed by competition with coal for heavy heating operations. The use of heavy fuel oils for carburetting not only results in substantial savings but also stabilizes the cost of manufacture of water gas by giving a carburetting material whose price depends upon the price of coal instead of the price of gasoline. Further the heavy-oil process is flexible enough to permit the use of a larger proportion of either oil or of solid fuel, depending upon the cost. Hence the gas manufacturer is able to take advantage of changes in the relative prices of coal, coke, or oil.

If it is attempted to employ heavy oils in the ordinary method of carburetting, the residue of carbon which results from the distillation and cracking of the oil in the carburetter causes a deposit on the checkerbrick which soon accumulates to a point when it is necessary to shut down the set and rechecker the carburetter. Also with fuels of high sulfur content the reaction between hydrogen sulfide in the gas and this hot carbon deposit on the checkerbrick results in the formation of carbon disulfide, which is not removed in the ordinary methods of gas purification and raises the organic sulfur in the gas beyond the allowable limit.

One method of overcoming these disadvantages of heavy oils was designed by the engineers of Stone & Webster, Inc.[110] In this process, the standard set is modified by the installation of a brick-lined pipe, which connects the top of the superheater to the gas offtake between the generator and the top hot valves, and by the installation of a hot valve in this line and an extra hot bottom valve, which allows part

107 Willien, L. J., *ibid.*, **1934**, **938**.

108 Richards, J. V., *ibid.*, **1930**, 1329–48.

109 Dashiell, P. T., *ibid.*, **1930**, 886–97; *Gas Age-Record*, **67**, 223 (1931).

110 Stewart, W. D., *Proc. Am. Gas Assoc.*, **1924**, 813–5, 885–6.

of the blow to be made with the generator completely isolated from the carburetter. In doing this the hot valves are reversed so that the top one is closed and the bottom is opened, the extra bottom hot valve is closed and the hot valve in the new connection to the top of the superheater is opened. The air introduced to the bottom of the generator heats the fuel bed, and the products pass through the new connection to the stack valve at the top of the superheater. At the same time the blast to the top of the carburetter burns the carbon from the carburetter checkerbrick which furnishes some heat to the carburetter and superheater. The modification was found successful on three 11-foot sets at Fall River, Mass., and Pawtucket, R. I.[111]

A second method proposed for the use of heavy oils utilized the reversed-air-blast process.[112] In this process,[113] the hot valves are removed, the bottom gas offtake is connected to the wash box, and valves are installed in the wash-box connections so that either the superheater or the bottom generator offtake may be shut off from the wash box. During part of the blow the air (reversed air blast) is introduced into the top of the superheater and passes back through the checkerbrick to the top of the generator fire. The rich producer gas during this period is led from the bottom of the generator to the wash box. The reversed air blast also serves to burn the carbon deposit from the checkerbrick of the carburetter.

In application of the reversed-air-blast process to the use of heavy oils, it was found necessary to change the spacing and arrangement of the checkerbrick in the carburetter and superheater.[112] In the resulting Western Gas reversed-air-blast-bunker oil process, oil is added to the generator only [114] but may be added either on the up-run or back-run. This process was installed in a number of plants [115] and used with oils of widely varying characteristics and with either coke or coke and bituminous coal mixtures. A modification, the *down-blast* process, is adapted to sets not equipped with a back-run pipe. In a later development,[116] heavy oils were combined with up to 70 percent of noncoking bituminous coal as generator fuel. Heavy oils with as much as 20 percent carbon residue have been found successful. In 1937, 45 installations of the Western Gas heavy-oil processes were in operation.[14]

One of the processes developed by the United Gas Improvement Company is the empty carburetter atomizing spray method,[117] in which the oil is introduced from a finely atomizing spray into an empty carburetter. The carbon residue from the heavy oil is therefore deposited on the sides and bottom of this checkerless carburetter, from which it may be removed partly by combustion during the blow and partly by mechanical means. To permit removal of the carbon the shell of the carburetter is fitted with a number of large self-sealing doors. In a hand-clinkered set, the carbon deposit may be largely removed from the empty carburetter while the generator fire is being cleaned. In a set with mechanical grate, a shutdown of about 1 hour a day is claimed to be necessary.

The second U.G.I. process is the marginal generator blast method of using heavy oils.[117] This also works on the principles of depositing the distillation residue of the heavy fuel oil where it will not interfere

111 Stewart, W. D., *ibid.*, **1925**, 1222.

112 Davis, R. F., *ibid.*, **1931**, 1150–2.

113 Howard, A. C., *Am. Gas Assoc. Monthly*, **7**, 579–84 (1925).

114 Hartzel, F. W., and Lueders, C. J., *Proc. Am. Gas Assoc.*, **1932**, 883–9.

115 Merritt, M. H., *ibid.*, **1933**, 824.

116 Merritt, M. H., *ibid.*, **1934**, 953.

117 Dashiell, P. T., *ibid.*, **1930**, 886–97.

with the operation of the set. This object is accomplished by spraying the oil over the top of the generator fire, where it is either burned during the blow or converted to blue gas during the run. To provide heat for vaporizing the oil on the top of the fuel bed the marginal generator blast is provided by means of a bustle pipe and tuyères to introduce secondary air at a number of points around the periphery of the fire about 1 foot below the normal top. The oil spray need not be of the atomizing type and should deliver the oil evenly near the periphery of the fuel bed. Good results are obtained with a rose type of spray which delivers the oil in fine streams that strike the fire within 18 inches of the outer edge.

The U.G.I. heavy-oil process permits four choices in the use of one or a combination of the two methods just described.[118]

1. When the generator fuel is low in price and the oil is high in price but of good quality, as much of the necessary oil as possible is introduced into the empty carburetter on the up-run. If more oil is needed to maintain the heating value of the gas, it is added to the top of the generator fire on the up-run only and the blow-run is omitted.

2. When the generator fuel is low in price and the oil is inferior in quality but high in price, oil must be added to the top of the generator fire as well as to the empty carburetter, but only on the up-run, and again the blow-run is omitted.

3. When the cost of fuel oil is low compared with the relatively high cost of generator fuel, as much oil as possible should be used. This is accomplished: (a) by introducing as much oil as possible into the empty carburetter on the up-run, adding enough oil to the generator on the up-run

to give the required heating value, and retaining the blow-run; (b) by using some oil in the carburetter on the up-run and additional oil in the generator on both the up-run and the back-run. The vapors of the oil added during the back-run are largely cracked to hydrogen by their passage down through the fire and thus increase considerably the volume of gas made from the oil.

4. The operation may be adjusted so as to take advantage of the large amount of tar formed from the heavy oil and produce tar with special properties as a valuable byproduct. Something along this line has been done with the straight-shot oil-gas process at Portland, Ore.,[119] and at Seattle, Wash.,[120] but details on the method in the water-gas apparatus are not available.

The great flexibility of the method of operation in the U.G.I. heavy-oil process may be illustrated by results obtained with an 11-foot back-run set using byproduct coke and Bunker C oil (11 percent carbon residue) and making 530-Btu gas. The results varied from 22.8 pounds of generator fuel and 3.30 gallons of oil per 1,000 cubic feet when no blow-run was used, to 15.8 pounds and 4.18 gallons with about 18 percent of blow-run gas. In this range, the capacity of the set increased from 4.5 to 5.75 million cubic feet per day, while the specific gravity of the gas increased only from 0.63 to 0.68.

Other modifications in apparatus and method of operation which have resulted from the use of heavy oil as carburetting material include: the Gas Machinery Company heavy-oil process[121] in which the oil is introduced into both the generator and carburetter; the introduction of a brick

[118] Harvey, W. J., *ibid.*, **1931**, 1159–63.

[119] Hall, E. L., *Gas*, **14**, 36 (1938).

[120] Effinger, R. T., *Gas Age-Record*, **81**, 28–9 (1938).

[121] Steinwedell, W. E., *Proc. Am. Gas Assoc.*, **1931**, 1209–10.

pier in the checkerless carburetter to increase the heat available for gasifying heavy oil in this apparatus; [122] the ignition arch process; [114] and the refractory-screen carburetter.[123]

In the Semet-Solvay ignition arch process, the checkerbrick with supporting tile and arches are omitted in the carburetter. Instead, two arches are sprung across the carburetter at right angles to each other, one just above the other. These ignition arches are near the top of the carburetter, and the wall on top of each arch is built up even with the bottom of the inlet connection from the generator. For the introduction of oil, four water-cooled atomizing sprays are located equally spaced around the circumference of the carburetter below the ignition arches. These sprays point upward at an angle of about 30 degrees so that the oil is discharged towards the bottom of the arches and countercurrent to the flow of the blue gas passing downward in the carburetter. In the process, oil is also sprayed over the top of the fire in the generator. During the blows secondary air is admitted partly to the top of the carburetter and partly through scurfing slots in the bottom of the carburetter. The oil is introduced into the carburetter during the up-runs and on the top of the generator fire during the back-runs. The operation of this process is further described in an article by Ide.[124]

The refractory-screen carburetter,[123, 125] a modification of the refractory-screen oil-gas process, was developed by the Improved Equipment-Russell Engineering Corporation to meet the requirements of heavy oil and coke in the manufacture of low-heating-value manufactured gas. In it the checkers in the carburetter are replaced by a shallow screen of small refractory blocks. In operation this screen receives and retains the carbon from the heavy oil which is sprayed into the carburetter. During the blow period, air introduced into the top of the superheater passes up through the carburetter screen for a short time. This air aids the regular secondary air, which passes down through the screen, in burning the accumulated carbon.

Terzian Factor. Study of data accumulated in the development and application of the U.G.I. heavy-oil process led to a new formula for relating the generator fuel and heavy oil to the heating value of the gas made:

$$\text{Terzian factor} = \frac{K}{A}$$

where $K = 10$ (pounds of fuel per 1,000 cubic feet) $+ 100$ (gallons of oil per 1,000 cubic feet), and $A =$ Btu per cubic foot of gas made. The value of this factor is generally between 1.0 and 1.35, varying directly with the gallons of tar formed per 1,000 cubic feet of gas made. On account of this direct relation with the tar formed the Terzian plant constant is found by the formula

$$\text{Terzian plant constant} = \frac{K_1}{A}$$

in which $K_1 = K - 100$ (gallons of tar per 1,000 cubic feet). The value of the Terzian plant constant is generally close to 0.9. For a discussion of data, charts, and examples illustrating application of these relations, reference should be made to the original article,[126] but the following conclusions seem warranted.

1. There is a distinct relation between

122 Parke, W. B., *ibid.*, **1934**, 897–908. Beard, W. K., *ibid.*, **1935**, 770–1.

123 Barclay, T. B., *ibid.*, **1935**, 783–4.

124 Ide, A. J., *Gas*, **16**, No. 5, 45 (1940).

125 Barclay, T. B., *Proc. Am. Gas Assoc.*, **1939**, 592–3.

126 Terzian, H. G., *ibid.*, **1936**, 848–60.

the calorific value of the gas, the generator fuel, oil, and tar results, even though the fuel and oil results might vary considerably on account of re-forming and the use of the blow-run and the air purge.

2. Where the generator fuel and oil used are fairly uniform in quality, the relation of the heating value of the gas, generator fuel, and oil results can be represented by the Terzian factor.

3. Experience shows that the Terzian factor is a practical means of comparing plant operating results (excepting the tar product) obtained under widely varying conditions of operation with heavy oil and with variations ranging in fuel from 10 to 25 pounds per 1,000 cubic feet, in oil from 3 to 6 gallons, and in heating value from 400 to 700 Btu per cubic foot.

4. There is a definite relation between the Terzian factor and the enriching value and tar-making properties of a heavy oil. Either the enriching value of the oil or the Terzian factor having been determined, it is then possible to predict the fuel and oil results throughout their range of variations, and the tar formed (but not its quality) per 1,000 cubic feet. Thus all the plant operating data necessary to evaluate a heavy oil, except the quality of the tar formed, are obtained.

5. The Terzian plant constant combines in a useful form the relation between the heating value of the gas, the fuel, oil, and tar results for making carburetted water gas with heavy oil.

Cold Carburetion. Refinery oil gas, when available, is desirable, from the standpoint of both economics and fuel conservation, as an enriching material in the production of water gas. As practiced by the Brooklyn Union Gas Company,[127] refinery oil gas having a specific gravity of 1.10 and heating value of 1,700 Btu per cubic foot is

mixed with the water gas ahead of the sulfur purifiers. When blue gas of 300 Btu and 0.55 specific gravity is enriched, the finished gas of 550 Btu and 0.65 specific gravity contains about 18 percent of the oil gas. Refinery oil gas may also be added, before the exhauster, to the water gas which has been partly enriched with oil.[128]

The cold carburetion of blue gas with butane or propane was reported as early as 1927.[129] It is economical only under special conditions such as meeting large peak loads of short duration.[130] When the enriched blue gas is a high-heating-value gas as a substitute for natural gas, enrichment with butane and propane gives a gas with burning characteristics near those of natural gas.[131]

The Young-Whitwell Back-Run Process. The back-run process, first developed at Everett, Wash.,[132] was the result of the attempt to utilize cheap local coal in the manufacture of gas.[133] It has since proved so widely successful with a variety of fuels, including coke, anthracite, and bituminous coal,[134] that it is almost standard practice in larger installations. It consists essentially in substituting, for the ordinary down-run, a back-run in which steam is admitted to the top of the superheater, passes down through the superheater up through the carburetter, and into the top of the generator through the gas offtake. The back-run gas made by passing this steam down through the fuel bed is led

127 Schaaf, A. H., *ibid.*, **1934**, 933–5.

128 Workman, D. M., *ibid.*, **1934**, 936–7.

129 Odell, W. W., *U. S. Bur. Mines, Rept. Investigations* **2840** (1927), 12 pp., *Bull.* **294** (1929), 96 pp.

130 Duesler, J. F., *Proc. Am. Gas Assoc.*, **1929**, 1807–11, **1930**, 1628.

131 Carpenter, F. T., *ibid.*, **1939**, 593–4.

132 Whitwell, G. E., *ibid.*, **1924**, 793–804.

133 Whitwell, G. E., and Young, D. J., *Chem. & Met. Eng.*, **29**, 664–9 (1923).

134 Anderson, A. H., *Proc. Am. Gas Assoc.*, **1925**, 1209–21.

through a special connection from the bottom of the generator directly to the wash box.

The changes in a three-shell carburetted-blue-gas apparatus necessary to convert it for the back-run are: (1) The upper hot valve and the connection of the bottom gas offtake to the hydrogen pipe are removed. The lower hot valve may be left and used as the back-run valve, or it too may be removed. (2) The bottom of the generator is connected by a back-run gas offtake to the inlet of the wash box. (3) The steam line to the top of the generator is replaced by one to the top of the superheater. The stack valve may have to be weighted to withstand extra pressure. (4) Valves are provided in the back-run pipe and in the gas connection between the superheater and the wash box so that gas may be caused to enter the wash box either from the superheater or from the bottom of the generator through the back-run pipe. A special three-way valve at the entrance to the wash box may be substituted for the two valves in the back-run and superheater connection pipes.

The method of operation with the back-run varies with the fuel and other conditions, the cycle being adjusted to give the most satisfactory condition of the fire. A cycle which the inventors found useful consisted of 2 minutes' blow with secondary air to the carburetter, 2 minutes' up-run with introduction of oil, 2 minutes' blow with secondary air to the carburetter, 2 minutes' back-run during which coal was charged to the generator by means of an automatic charger, and then a 1-minute up-run, after which the cycle was repeated. Brief blow-purges are also desirable. To go from the blow to a back-run, the carburetter and generator blast valves are closed as usual. With the valve on the gas connection from the superheater to the wash box closed, the valve on the back-run connection to the wash box is opened as soon as the blast is shut off. The stack valve is then closed and the steam to the top of the superheater turned on. The steam passes down through the superheater and up through the carburetter to the top of the generator and down through the fire. The blue gas made passes through the back-run connection from the bottom of the generator directly to the wash box. Before going on the blow after a back-run, it is necessary to reverse the steam and valves in the gas offtake so as to make a regular up-run with bottom steam long enough to purge the blue gas from the base of the generator; otherwise an explosion would result when the generator blast is turned on. When gas oil is used the oil rate is increased to introduce all the oil during the up-run and no oil is used in the back-run. With heavy oils, as already noted, part of the oil may be put on the top of the generator fire during the back-run.

Operating results with the back-run will be stated later. The advantages found for this process include:

1. Since the heat losses of the set are reduced there is a corresponding reduction in the generator fuel required per 1,000 cubic feet of gas made. The back-run steam cools the top of the superheater and itself is highly superheated by the passage through the checkerbrick on its way to the top of the generator. It, therefore, cools the fire less in the formation of blue gas. On the other hand the back-run gas and undecomposed steam leave the bottom of the generator and enter the wash box at a temperature of 800° F or lower instead of 1,200 to 1,400° F, which is the temperature of the regular down-run gas when it enters the wash box from the superheater. The back-run gas therefore carries less heat

away from the set and throws a smaller load on the condensing apparatus. Also the back-run steam cools the checkerbrick of the top of the superheater so that the brick extract more heat from the up-run gas and blast products, which therefore carry less heat away from the set. These savings, though partly offset by the decrease in the steam made by the waste-heat boiler, result in a considerable reduction in the generator fuel on account of the shorter blasting periods made possible. The cool superheater top also decreases the lampblack and naphthalene formed by overcracking of the oil.

2. The back-run steam reacts with any carbon deposited on the checkerbrick and keeps them clean, thus lengthening the life of the checkerbrick and saving labor, operating time, and materials by the longer periods betweer recheckerings. Since carbon is removed from the carburetter checkerbrick by the back-run steam, it is possible to operate with high-sulfur heavy oils in this process without the checkerbrick becoming clogged and without excessive organic sulfur in the gas.

3. On account of the larger ratio of run to blow and the less frequent shutdowns for recheckering, the capacity of the set is increased.

4. Because the make gases enter and leave the wash box at lower temperatures, the condensing capacity of the plant may be materially decreased.

5. The elimination of the hot valves removes a constant source of expense and trouble in maintenance.

6. With an automatic charger in the back-run process, the use of smaller sizes of cheaper fuel is possible.

Semet-Solvay Reverse-Flow Water-Gas Machine.[135] In this process two modifications in the principle of operation of the

water-gas process are introduced. First, the heating gases in the superheater are caused to flow down through the checkerbrick so as to take advantage of the phenomena of convection currents which have been found of special importance in the heating of checkerbrick in the Pacific Coast oil-gas process [136] and in the heating of blast-furnace stoves.[137] Second, the gases pass up through the carburetter, so that during the up-run the oil which is introduced by an atomizing spray into the top of the carburetter meets a rising current of hot blue gas and the evaporating droplets fall through the upward current of gas towards the hotter zone in the bottom of the carburetter.

As shown in Fig. 11, this is a three-shell machine with the conventional generator. The hydrogen pipe from the top of the generator leads to the bottom of an elevated carburetter. The carburetter outlet is at the top and connects to the top of a standard-size superheater. The superheater outlet is at the bottom and connects by a riser pipe to the stack valve and a three-way back-run valve located above the wash box as in normal practice. A back-run pipe extends from the base of the generator to the three-way back-run valve. Near the bottom of the carburetter, supporting tile carry three or four rows of standard checkerbrick. Above them the carburetter is empty, but the superheater contains the usual number of checkerbrick. An atomizing oil spray is installed in the top of the carburetter, and for heavy-oil operation a spray is provided to introduce additional oil in the top of the generator.

In the operation during the blow period,

135 Oliveros, R. P., *ibid.*, **1936**, 827–30.

136 Cowles, R. R., Henderson, W. M., and Yard, W. S., *Production of Oil Gas*, Educational Committee of Public Service Employees' Assoc., San Francisco, 1922, 96 pp.

137 Groume-Grjimallo, W. E., *Iron Age*, **107**, 1613–6 (1921).

PLAN VIEW

ELEVATION - SECTION A-A
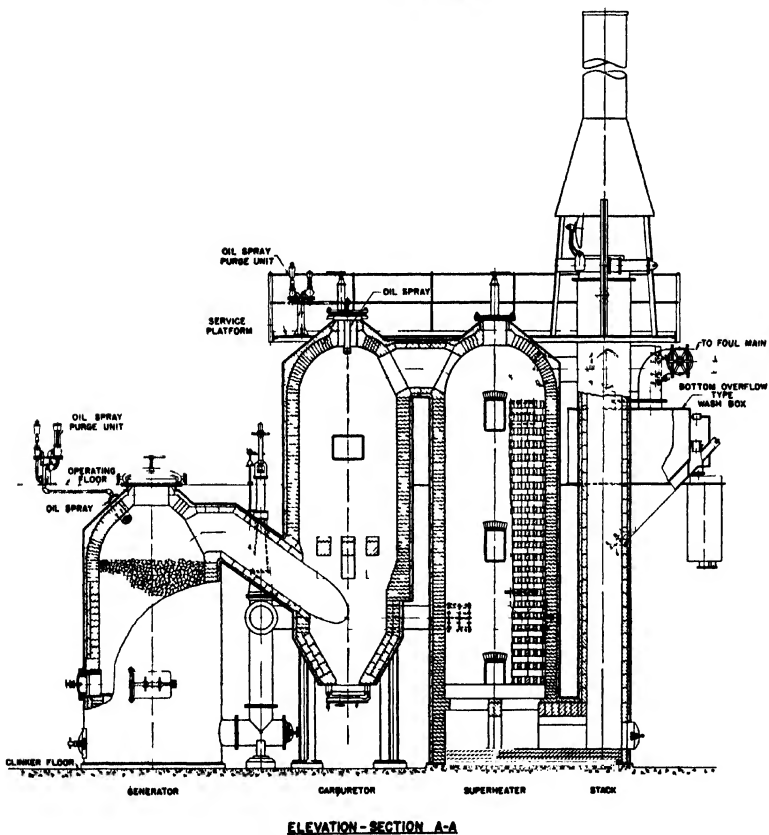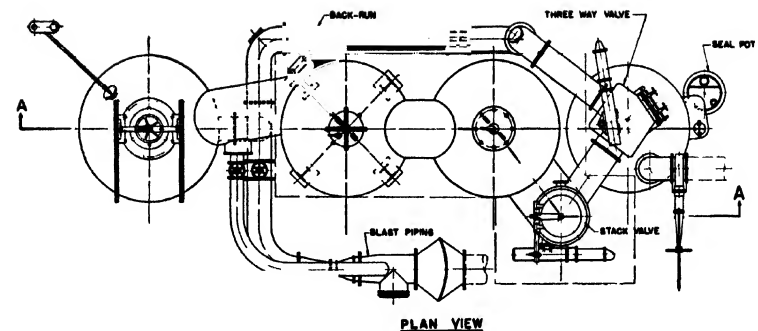
FIG 11   The Semet Solvay reverse flow water-gas machine for light or heavy oil operation, coke or bituminous coal.

primary air admitted in the base of the generator passes up through the fuel bed. Secondary air is admitted at the top of the generator or in the connection between the generator and carburetter. Combustion of the blast gases heats the checkerbrick grate at the bottom of the carburetter and makes this the hottest part of the carburetter. The blast products then pass up through the carburetter, down through the superheater, and up the riser pipe to the stack. In the superheater, convection currents cause the hotter gases to lag behind the downward main current of the heating gases and thus facilitate even heating and efficient heat transfer.

In gas-making, during the up-run, steam is admitted at the base of the generator and the blue gas passes from the top of the fire to the bottom of the carburetter and upward through the hot zone of the checkers. At the same time oil is sprayed into the top of the carburetter, and the droplets travel down against the upward current of hot blue gas. As the oil gasifies, it is carried along with the blue gas. The ungasified droplets travel downward against rising currents of hot blue gas and into hotter regions until the gasification is complete, except for the residual carbon which deposits in a thin layer on the few checkerbrick at the bottom of the carburetter. The mixture of blue gas and oil gas and vapors passes from the carburetter down through the superheater, where conversion into permanent gases is completed. The gases leave the bottom of the superheater where the temperature is lower and pass up the riser pipe to the wash box.

During the back-run, steam is admitted at the bottom of the superheater, passes up through the superheater, down through the carburetter, and to the top of the generator. The back-run gas passes from the bottom of the generator to the wash box

as in the standard back-run apparatus. During the back-run some blue gas is made from any carbon which has been deposited on the checkers at the bottom of the carburetter, and this action together with the combustion at this point during the blow consumes the carbon which is deposited here in heavy-oil operation. The operation of this process with heavy oil has been described in detail by Dopp,[138] and the use of this process in the production of high-Btu gas has been discussed by Vittinghoff.[139]

Low-Gravity Water Gas. Work done at Philadelphia in 1910, leading to a patent by G. H. Waring in 1911, showed that carburetted blue gas containing up to 75 percent hydrogen and having a specific gravity as low as 0.25 could be made. Oil and no steam was introduced during the down-run with a low hot fire, and the second half of the run was up-run with steam and no oil. The object was to obtain gas for balloons, and no commercial application was made of the process.[140] In 1926, the necessity at St. Paul, Minn., of finding a peak-load gas which could be substituted for or mixed with coke-oven gas led to further work on the subject in a back-run water-gas apparatus.[141] The Willien-Stein process which resulted was taken over by the United Gas Improvement Company.[142]

In the earlier work at St. Paul with an 11-foot back-run set, to make 550-Btu gas, about 1.5 gallons of gas oil per 1,000 cubic feet was introduced into the carburetter during the back-run and the vapors were cracked by passing down through the gen-

[138] Dopp, J., paper presented at Joint Conf. of Prod. and Chem. Com., Am. Gas Assoc., 1939.

[139] Vittinghoff, H., *ibid.*, 1938.

[140] Evans, O. B., *Proc. Am. Gas Assoc.*, 1929, 1219–21.

[141] Willien, L. J., and Stein, L., *ibid.*, 1927, 1036–45.

[142] Hall, E. L., *ibid.*, 1930, 1491–2.

erator fire. The rest of the oil was put into the carburetter as usual on the up-run. In this way the specific gravity of the water gas was reduced from 0.70 to between 0.50 and 0.55. This gas was successfully used in a district where the appliances were adjusted for coke-oven gas. Better results were obtained with coke or a mixture of coke and coal than with all bituminous coal. The capacity was increased 23 percent over that with coke and 57 percent over the capacity of normal operation with bituminous coal.

Later work at Philadelphia [140] showed that it was possible to reduce the specific gravity of water gas from 0.65 to 0.55, with an increase in capacity and at an increased cost of somewhat less than 3 cents per 1,000 cubic feet of 530-Btu gas. In this work, the oil was introduced into the top of the superheater on the back-run. Reduction of the specific gravity below 0.55 would be relatively more expensive. This process has no effect on the amount of hydrogen sulfide or of organic sulfur in the gas but apparently increases the naphthalene and increases the free carbon in the tar. In operation over long periods, some provision should probably be made to take care of the lampblack produced. The process has also been tested at Louisville, Ky., at Pontiac, Mich., and again at St. Paul.[143] A typical low-gravity gas made in a back-run set is: [142]

	PERCENT
Carbon dioxide	3.6
Illuminants	6.1
Oxygen	0.4
Carbon monoxide	21.9
Methane	10.9
Ethane	2.5
Hydrogen	49.6
Nitrogen	5.0
Btu per cubic foot	536
Specific gravity	0.538

The fact that the Willien-Stein process gives increased capacity to standard equipment and also furnishes a gas which approaches coal gas in burning characteristics makes the process of special interest.

High-Btu Water Gas. With the spread of the transmission of natural gas in manufactured-gas territories, the necessity arose of producing gas which could be mixed with or even substituted for natural gas. Since in many of the places thus affected water-gas apparatus was already available, these conditions led to the manufacture of high-heating-value carburetted blue gas. The details of operation depend on local conditions.[181, 144]

In general the manufacture of high-heating-value gases in the water-gas apparatus has been well summarized by Nagler.[145] Essentially, high-Btu water gas is made by greatly increasing the proportion of oil gas and correspondingly decreasing the blue gas in the mixture. To increase the proportion of oil gas, the oil used is raised from about 3 gallons per 1,000 cubic feet of 530-Btu gas to some 7.5 gallons for 800-Btu gas and as much as 10 to 13 gallons for 1,000-Btu gas. On account of the smaller proportion of blue gas the steam input may be decreased from about 30 pounds per 1,000 for 530-Btu gas to 15 to 20 pounds for 800-Btu and 10 to 15 pounds for 1,000-Btu gas. In certain types of operation, a large amount of additional "carrier steam" may be introduced to the top of the generator during an oil run.[146]

Gas Age-Record, **64**, 717–8, 720 (1929). Stein, L., *Proc. Am. Gas Assoc.*, **1930**, 1490–1502.

[144] Fischer, E. L., *ibid.*, **1933**, 789–93. Young, H. B., *ibid.*, **1933**, 795–6. Dieterle, E. A., *ibid.*, **1933**, 806. Willien, L. J., *Gas Age-Record*, **72**, 431–3, 440–1 (1933). Workman, D. M., *Proc Am. Gas Assoc.*, **1934**, 928–30. Beard, W. K., *ibid.*, **1935**, 768–72. Steinwedell, W. E., *ibid.*, **1938**, 681. Azar, A. A., *ibid.*, **1938**, 682–3.

[145] Nagler, K. B., *ibid.*, **1933**, 805.

[146] Beard, W. K., ref. 144.

[143] Willien, L. J., *ibid.*, **1929**, 1221–3, 1223–6 ;

The generator fuel remains approximately the same or may be decreased somewhat, 25 to 30 pounds per 1,000. The temperatures in the superheater range from 1,350 to 1,400° F.

Of the 7.5 gallons of oil per 1,000 cubic feet for 800-Btu gas about two-thirds are introduced into the carburetter and one-third onto the generator fire during the up-run. For 1,000-Btu gas, approximately one-fourth of the 13 gallons of oil may be put into the generator, or with the use of a pier in a large carburetter all the oil may be put into the carburetter.[146] The specific gravity of the gases is given in Table IX. To obtain lower specific gravities,

sets and as much as 50 percent for small sets. In making higher-Btu gas the output of the set may be considerably reduced.

Peak-Load Gases. It has already been indicated that the manufacture of high-heating-value carburetted blue gas usually has the object of meeting peak loads. Hence the previous discussions and references on that subject apply equally here. Additional discussions from the special standpoint of peak-load capacity are found in papers by Pratt and Willien.

Pratt [147] presented some interesting figures on the capacities of water-gas apparatus. In 1910, the rated capacity of an 11-foot water-gas set was 2,000,000 cubic

TABLE IX

COMPARISON OF CARBURETTED BLUE GASES OF DIFFERENT HEATING VALUES [145, 146]

Btu/cu ft	540	695 *	811	850	1,010
Oil, gal/1,000 cu ft	3.0	4.2	7.5	8.6	13.1 †
Fuel, lb./1,000 cu ft	30.0	30.8	32.1	32.0	26.5
Steam, lb/1,000 cu ft	30.0	30.9	20.0	19.8	15.0 ‡
Carbon dioxide, percent	3.4	4.3	1.8	1.6	4.4
Illuminants, percent	8.4	12.6	19.7	18.9	27.4
Oxygen, percent	1.2	0.7	0.3	0.2	1.1
Carbon monoxide, percent	30.0	30.2	25.7	21.3	9.1
Hydrogen, percent	31.7	29.3	29.2	28.0	19.9
Methane, percent	12.2	17.8	13.5	20.7	21.8
Ethane, percent	....	....	5.2	4.3	5.3
Propane, percent	....	....	....	....	0.3
Nitrogen, percent	13.1	5.1	4.6	5.0	10.7
Specific gravity	0.64	....	0.70	0.69	0.85

* 23.5-candlepower gas.
† Heavy oil, 7.6 percent Conradson carbon, specific gravity 13.7 °Baumé.
‡ In addition 42 pounds of steam per 1,000 cubic feet was used in the top of the generator as carrier steam and 36 pounds per 1,000 cubic feet of exhaust steam as superheater cooling steam.

some of the oil gas must be re-formed by adding oil on the fire during the back-run or down-run. The tar yield is markedly increased from the 0.2 gallon per 1,000 for 530-Btu gas to about 1.1 gallons for 800-Btu and some 30 percent of the oil used for the 1,000-Btu gas. The thermal capacity of the apparatus in making 800-Btu gas may be increased 15 to 20 percent for large

feet per day. Since then the capacities have been increased by the use of higher blast pressures, hydraulic and automatic valve operation, larger connections, down-run and back-run methods of operation, automatic charging, and mechanical grates, so that in 1930 the capacity of an 11-foot

147 Pratt, C. O., *Proc. Am. Gas Assoc.*, **1930**, 1496–502.

set with mechanical generator was upwards of 4,500,000 to 5,000,000 cubic feet per day and of a 12-foot set similarly equipped up to 8,000,000.

Starting with the capacity of a water-gas apparatus operated with bituminous coal and making 540-Btu, 0.57-specific gravity gas as a basis, Pratt calculated that the capacity could be increased as follows:

	PERCENT INCREASE IN CAPACITY
1. Using coke	25
Making 610-Btu gas from coke and diluting	
2. With producer gas	57
3. With blue gas	67
4. Using butane in carburetter for enrichment with coke	60
5. Mixing 4 with producer gas cold enriched with butane	148

Attention has also been called to the Willien-Stein process for making low-gravity water gas for substituting for coal gas in peak loads, and for increasing capacity by enriching low-gravity gas with butane,[130] but capacity figures are not given. Willien[148] has discussed fully the methods for meeting peak loads under widely varying conditions, many of which involve use of blue gas or carburetted blue gas.

Operating Results. Some operating results have already been stated in the previous discussions. Others may be found in the reports of the water-gas committees of the American Gas Association. Operating results vary according to local conditions, but in general it may be said[149] that, when operating with ordinary gas oils and making 550-Btu gas, the quantities of materials required per 1,000 cubic feet of gas are as follows:

Generator fuel, pounds	26 to 33
Boiler fuel, pounds	
Without exhaust steam or waste-heat boiler	12 to 18
Without exhaust steam but with waste-heat boiler	9 to 14
Using exhaust steam and with waste-heat boiler	6 to 10
Air, cubic feet at 60° F and 30 inches	
With coke or anthracite	1,400 to 1,800
With bituminous coal	1,000 to 1,400
Steam, pounds	
Decomposed	15 to 20
Undecomposed	15 to 25
Total used in generator	30 to 45
Oil, gallons	2.95 to 3.55
Percent of total heat in fuel, oil, and steam recovered in heating value of the gas	67 to 56

For comparison, results which were obtained from 11-foot back-run sets in the same plant operating with ordinary gas oil and with Bunker C heavy fuel oil are shown in Table X.

Operating results for one year of six 12-foot sets equipped with back-run U.G.I. mechanical generators and U.G.I. heavy-oil system show:[150]

Heating value of gas, Btu per cubic foot	540
Generator fuel, pounds per 1,000 cubic feet	10.9 to 20.1
Average	15.3
Oil, gallons per 1,000 cubic feet	3.7 to 4.7
Average	4.2
A.P.I. of generator oil	12.6 to 24.7
A.P.I. of carburetter oil	14.7 to 22.0
Conradson carbon	4.2 to 11.7
Percent re-formed	0 to 40

Two years' operation of eight U.G.I. cone-top water-gas sets, with hand-clinkered generators, 9-foot internal diameter, back-run, checkerless carburetters, waste-

148 Willien, L. J., *ibid.*, **1935**, 22–7.
149 Battin, W. I., private communication, 1926.
150 Kellogg, R. M., *Proc. Am. Gas Assoc.*, **1933**, 797.

TABLE X

COMPARISON OF RESULTS WITH GAS OIL AS AGAINST BUNKER C OIL IN THE SAME PLANT [118]

	Gas Oil	Bunker C Oil
Gravity of oil, Baumé	24.0	15.3
Generator fuel	Coke	Coke
Generator fuel, pounds per 1,000 cubic feet	26.2	15.8
Oil, gallons per 1,000 cubic feet	2.90	4.18
Steam to sets, pounds per 1,000 cubic feet	38.0	30.3
Heating value of gas, Btu	535	535
Specific gravity of gas	0.62	0.68
Hydrogen sulfide in crude gas, grains per 100 cubic feet	120	260
Residuals, gallons:		
Tar per 1,000 cubic feet	0.72	0.92
Tar per gallon of oil	0.25	0.23
Drip oil per 1,000 cubic feet	0.06	0.08
Drip oil per gallon of oil	0.02	0.02
Capacity per set per day, thousands of cubic feet	4,500	5,700

TABLE XI

OPERATING DATA FOR EIGHT U.G.I. CARBURETTED-WATER-GAS SETS [151]

Gas made, million cubic feet	20,606
Btu per cubic foot average	530
Specific gravity, average	0.69
Per set per day, 1,000 cubic feet	5,847
Coke, pounds per 1,000 cubic feet, average	12.40
Boiler fuel, pounds per 1,000 cubic feet, average	5.10
Oil, gallons per 1,000 cubic feet, average	4.22
Percent to generator	60
Percent to carburetter	40
Percent re-formed	25
A.P.I. gravity	19.5
Coke residue	5.4
Steam to set, pounds per 1,000 cubic feet, average	19.5
Operating cycle, minutes	4.0
Blow, percent of cycle	33
Blow-run	8
Up-run	37
Back-run	20
Air purge	2

heat boilers, and steam accumulator gave the data shown in Table XI.[151]

In Table XII, data obtained in six plants on heat balance of the carburetted-blue-gas process are given. Data of plants A, B, and C are from the report of the American Gas Association Subcommittee on Test Code for Water Gas Plants.[152] The information on plants D and E was given by Harvey [118] and for plant F by Eck.[151]

PROPOSED WATER-GAS PROCESSES

A number of processes, some of which may have found use in other countries, have not yet been employed commercially in the United States. These processes utilize the following principles of operation: (1) continuous production of water gas by

heating the reaction chamber through conducting walls, by supplying the heat with gas mixed with the steam, or by the passage of electric currents through the reacting fuel; (2) continuous production of semi-water gas with steam and oxygen or oxygen-rich mixtures; and (3) gasification of fine-grained fuel with steam. Most of the processes employ combinations of these principles, and many of them achieve complete gasification.

Continuous production of water gas in an externally heated reaction chamber was the basis of the earliest processes, but, with lump fuel and poorly conducting refractory walls, these processes were never satisfactory and were quickly displaced when intermittent heating of the fuel bed was introduced. Some attempts have been made to revive this method of operation.

151 Eck, L. J., *ibid.*, **1934**, 938–41.
152 Genay, T. B., *ibid.*, **1930**, 1523–9.

TABLE XII

HEAT BALANCE OF CARBURETTED-BLUE-GAS PROCESS

	A [152]	B [152]	C [152]	D [118]	E [118]	F [151]
Size of set, external diameter of generator, ft	11	11	9	11	11	11
Average depth of fuel, ft	7.5	10.5	8.0	....	....	....
Duration of test	1 year	1 month	24 hours	....	....	2 years
Gas made, million cubic feet per set per day	2.4	3.6	1.8	4.5	5.7	5.8
Btu per cubic foot	600	530	520	535	535	530
Generator fuel	Coke and gas coal	Coke	Bituminous coal	Coke	Coke	Coke
pounds per 1,000 cu ft	30.6	27.7	28.7	26.2	15.8	12.4
Oil used, A.P.I. gravity	32.0	24.0	36.0	24.2	15.3	19.5
gallons per 1,000 cu ft	3.68	2.98	2.59	2.90	4.18	4.22
Steam, pounds per 1,000 cu ft	54.0	51.8	17.1	38.0	30.3	19.5
Steam from waste-heat boiler, pounds per 1,000 cu ft	....	20.5	....	....	....	13.0
Temperature of make gases leaving set, °F	1,300	1,100	....	....	....	....
of blast products leaving set, °F	....	1,110	....	....	....	....
of stack gases leaving waste-heat boiler, °F	....	450	....	....	....	....

Percent of Total Heat Input

	A	B	C	D	E	F
Input						
Generator fuel	40.78	39.4	51.3	41.8	23.3	19.5
Enriching oil	52.94	53.1	44.6	52.3	72.8	77.8
Steam, total heat	6.28	7.1	4.1	5.9	3.9	2.7
Feed water	....	0.4	....	....	....	...
	100.00	100.00	100.00	100.00	100.00	100.00
Output						
Heating value, gas	61.88	64.7	67.0	65.8	61.1	63.8
tar	7.89	12.3	10.6	13.5	15.3	17.0
drip oil	0.65	1.1	....	1.0	1.4	0.9
	70.48	78.1	77.6	80.3	77.8	81.7
Sensible heat, in gas	3.06	2.8	2.0	....	....	....
in tar	0.36	0.6	0.3	....	....	....
in drip oil	0.02	....	....	....	....	....
in dry blast products	5.53	1.8	4.3	....	....	....
Combustible in stack gases	0.35	0.4	2.7	....	....	....
Total heat in undecomposed steam and water vapor	5.41	5.8	6.4	....	....	....
Combustible in refuse	1.30	1.9	2.4	....	....	....
Steam in waste-heat boiler	....	2.9	....	....	....	1.6
Radiation and unaccounted for	13.55	5.7	4.3	....	....	....
	100.00	100.00	100.00	....	....	....

The Heller process [153] gasifies powdered coal with steam in large-diameter, small-altitude, cylindrical reaction cells heated from both flat sides by similar combustion cells. The apparatus consists of a cylindrical shell with axis horizontal and divided by partitions perpendicular to the axis into five compartments, two reaction and three combustion cells, arranged alternately like grindstones placed against each other on the same horizontal axle. A pair of distributing flues supply preheated air and producer gas to each combustion cell through nozzles arranged side by side around the periphery of the cell. At the top the combustion cells are connected to a common waste-gas flue. Each reaction cell is provided with a fuel inlet and a number of steam inlets placed at intervals around the circumference of the cell. These inlets inject both the steam and powdered fuel tangentially. The reaction cells are connected to a central flue through which the water gas and fine ash are withdrawn to a cyclone dust catcher. In a week's operation of a trial unit at Tegel works of the Berlin Gas Company, a noncaking bituminous coal with 25.6 percent volatile matter and 12 percent ash was used. Average 24-hour results were: input of 1.7 tons of coal giving 161,000 cubic feet of 304-Btu-per-cubic-foot blue gas; producer gas used for heating, 216,000 cubic feet of 134 Btu per cubic foot; steam used, 3,380 pounds; producer efficiency, 64.5 percent; and thermal efficiency, 61 percent. It was said that a commercial plant for a capacity of 520,000 cubic feet per day had been designed.

McAuliffe [154] has patented the injection of pulverized coal and steam into a narrow vertical retort with large flat walls heated to 1,500–1,600° F by flues. Herzberg [155] proposed injection of powdered fuel with steam into externally heated chambers of coke-oven size. Schmidt and Groh [156] have discussed the use of highly conductive steel tubes for the continuous production of water gas and have described the operation of a technical-scale apparatus with a capacity of 70,000 cubic feet per day.

Continuous production of water gas with internal electrical heating has been claimed by Stitzer.[157] The apparatus consists of a vertical retort of square cross section, divided at the top into inner and outer zones by a gas-impervious inner retort open at the bottom above the heating zone. Coke is charged at the top into the outer zone and coal into the top of the inner zone. The heat is supplied by the electric current which passes horizontally across the heating zone. The current is regulated to furnish heat to carbonize the coal in the top inner zone and to heat the coke in the heating zone to the temperature for the water-gas reaction. Steam introduced at the bottom serves to cool the coke below the heating zone, to form water gas with the coke in the heating zone, and to carry heat up to the coal and coke above. An inert gas introduced into the top of the inner zone carries away the distillation gases. The gas produced is a mixture of the inert gas, water gas, and the distillation gases.

Winkler [158] has patented a process to form water gas by electrically heating fine fuel with electrodes in the fuel and by passing steam up through the heated fuel

153 Thau, A., *J. Inst. Fuel*, **5**, 1–20 (1931); *Gas Engr.*, **48**, 315–22 (1931). Brownlie, D., *Gas Age-Record*, **68**, 220–4 (1931).

154 McAuliffe, S. J., U. S. Pat. 1,780,759 (1930).

155 Herzberg, F., Brit. Pat. 367,363 (1930).

156 Schmidt, R., and Groh, E., *Braunkohlenarch.*, No. **44**, 50–8 (1936); *Oel Kohle Erdoel Teer*, **12**, 41–51 (1936).

157 Stitzer, R. B., U. S. Pat. 2,093,493 (1937).

158 Winkler, F., U. S. Pat. 1,857,799 (1932).

at a speed which gives a "boiling" motion to the fuel. Hole [159] has described the production of water gas by passing steam up through a vertical retort heated electrically with electrodes at top and bottom. A process has been claimed [160] in which coke activated with potassium hydroxide or iron oxides is heated electrically to 1,000° C to avoid clinker formation.

Heating with recirculated gases in the continuous production of water gas is the basis of the Pintsch-Hillebrand and the Koppers processes. In the Pintsch-Hillebrand process [161] recirculated water gas and distillation gases with steam (saturation temperature 60 to 74° C) are preheated to 1,280° C in checkerbrick regenerators. The heated mixture then passes through coked fuel where water gas is formed and the temperature is reduced to 700 or 750° C. Part of the gas at this point is drawn off through a washer and saturator, after which a portion is removed as product and the rest led back to the recirculation mixture for reheating. The other part of the water gas mixture from the reaction chamber passes on up through the fresh fuel where it chars the fuel, removes the distillation gases, and is cooled to about 400° C. This mixture of water gas and distillation gases is detarred in an electrical precipitator and combined with the recirculated portion of water gas and steam which are then forced by a blower through the regenerator to be preheated for the next cycle. A portion of the hot mixture may be used as fuel for heating the alternate regenerators in which it is burned with air. In a later develop-

ment [162] producer gas is used to heat the regenerators. The process requires fuel of high activity. It has been used at the Hamburg Gas Works in Germany.

The Koppers process also uses heating with recirculated gases. The heat-carrying gases, consisting of a mixture of steam, water gas, and distillation gases, are heated in a chamber which contains refractory gridwork and which is alternately heated by combustion of fuel gases.[163] The steam is furnished by evaporation of the moisture content of the fresh fuel, which also serves to cool the gases leaving the fuel below 250° C so that they may be mechanically accelerated on their way to the heating stage.[164] In the heating step, the hydrocarbons of the distillation gases react with steam to form water gas.[165] The heated mixture of gases is then introduced into the lower part of the generator and passes up through the coked fuel where water gas is formed. Part of the water gas is withdrawn from the central portion, and the rest passes on up through the fresh fuel (brown coal, lignite, etc.), causing distillation, and then is recirculated to the heating stage.[166] Temperatures are regulated so that the gases withdrawn at the top of the water-gas stage are a predetermined mixture of hydrogen, carbon dioxide, and monoxide.

Continuous gasification with steam and oxygen has been discussed to some extent in the section on producer gas (pages 1629–35). Of some additional interest is the plant built in 1936 to furnish city gas to Zittau in Germany. This plant with ca-

159 Hole, I., *Gas Industry*, **52**, 446 (1935); *Am. Gas J.*, **143**, 122 (1935).

160 Non-Poisonous Gas Holding Co., Ltd., Brit. Pat. 457.181 (1935).

161 Stief, F., *Gas- u. Wasserfach*, **75**, 581–6 (1932).

162 Stief, F., *ibid.*, **83**, 1–6 (1940).

163 Ramsey, A. R. J., Brit. Pat. 476,879 (1936).

164 Koppers, H., U. S. Pats. 2,148,298–9 (1939).

165 Radtke, M., U. S. Pat. 2,175,613 (1939).

166 Koppers, H., U. S. Pat. 2,137,723 (1938).

pacity of about 350,000 cubic feet per day operated under a pressure of 300 pounds per square inch and used a mixture of oxygen and steam superheated to about 900° F. The fuel was brown coal. About 62 pounds of steam and 150 cubic feet of oxygen were required per 1,000 cubic feet of finished gas. The raw gas contained 30.2 percent carbon dioxide, 16.5 percent carbon monoxide, 34.0 percent hydrogen, and 16.3 percent methane. Scrubbing under pressure removed most of the carbon dioxide, giving a gas with 3.0 percent carbon dioxide, 22.8 percent carbon monoxide, 48.7 percent hydrogen, 22.6 percent meth-ane, and about 480 Btu per cubic foot.[167]

Developments in continuous production of water gas from powdered fuel have largely followed the work of Winkler.[168] The principle underlying the process is agitation of the fine-grained fuel by means of the gasifying medium—an agitation which resembles boiling in liquid. For production of water gas a mixture of oxygen with steam is used, and, as indicated in the section of gas producers, the apparatus may work under considerable pressure.

167 Selden, R., *Ind. Eng. Chem., News Ed.*, **16,** 535 (1938) ; *Gas Age-Record,* **82,** 18 (1938).

168 Grimm, H. G., *Proc. 3rd Intern. Conf. Bituminous Coal,* **1,** 874–81 (1931).

HYDROGENATION OF COAL AND TAR *

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INTRODUCTION AND SUMMARY OF INDUSTRIAL DEVELOPMENT

The important chemical differences between coal and petroleum are the higher hydrogen and much lower oxygen and nitrogen content of petroleum. Processes that increase the hydrogen content of coal appreciably usually remove most of the oxygen and nitrogen. In 1869 Berthelot showed[1] that treatment of coal with 100 parts of hydriodic acid at 270° C for 24 hours yielded 60 percent (of the weight of coal used) of oil and 30 percent of a bitumenlike residue. The oil contained aromatic and naphthenic hydrocarbons. Similar results were obtained by Berthelot with dried wood and partly carbonized wood, but coke and graphite were not attacked by the hydriodic acid. The experiments of Berthelot were extended by Fischer and Tropsch,[2] who investigated the hydrogenation of coals of different geologic ages with the aid of hydriodic acid and phosphorus. These experiments, as well as those reported by Fischer,[3] in which sodium for-

mate was used, showed that the degree of liquefaction increased with decrease in rank.

In 1913, Bergius compared the action of hydrogen under pressure on coal with that on his synthetic coal produced by heating cellulose in an autoclave with water to 340° C at pressures of about 100 atmospheres.[4] In 1914, Bergius patented[5] the hydrogenation of coal and other solid carbonaceous material of vegetable origin by the use of hydrogen under pressure at temperatures between 300 and 500° C. The Bergin Aktien-Gesellschaft für Kohle und Erdöl-Chemie was formed in 1914 to investigate the process on a commercial scale. Owing to the war little progress was made until 1921, but by the end of 1922 a plant whose capacity was 1 ton of coal per day was in operation. It contained three reaction vessels connected in series, and was heated by gas-fired lead baths. In many respects, this plant was similar to that designed by Bergius for the destructive hydrogenation of oils and tars.[6] Bergius's plant consisted of a reaction chamber of 4-cubic-meter capacity and of double-walled construction so that hot compressed nitro-

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1 Berthelot, P. E. M., *Bull. soc. chim.*, (2), 11, 278–86 (1869) ; *Ann. chim. phys.*, (4), 20, 526–34 (1870).

2 Fischer, F., and Tropsch, H., *Ges. Abhandl. Kenntnis Kohle*, 2, 154–9 (1918).

3 Fischer, F., *The Conversion of Coal into Oils*, Ernest Benn, London, 1925, 277 pp.

4 Bergius, F., *J. Gasbeleucht.*, 54, 748–9 (1912).

5 Bergius, F., and Billwiller, J., Ger. Pat. 301,231 (1913) ; Brit. Appl. 18,232 (1914).

6 Bergius, F., *Z. angew. Chem.* 34, 341-47 (1921), 35, 626–27 (1922). Ger. Pats. 304,348 (1913), 303,893 (1914).

gen could be circulated through the jacket space. This mode of heating avoids hydrogen embrittlement of the pressure retaining wall. A pressure of about 100 atmospheres of hydrogen was used. Berginization of brown-coal producer tar in this apparatus at 400° C yielded [6] 25 percent (weight) of gasoline boiling in the range 75 to 210° C and 40 percent of middle oil boiling from 210 to 300° C. The residue was a pitch of 1.04 specific gravity and 15° C solidification point.

Bergius's procedure in coal hydrogenation was to mix the powdered coal with about an equal quantity of a heavy recycle oil produced in a previous hydrogenation and several percent of a titaniferous iron ore ("Luxmasse"). The temperature was about 480° C, and the pressure of hydrogen was 200 atmospheres. In 1925–6 Bergius [7] gave the yields of oil and solid residue obtained in about 120 laboratory 2-liter bomb tests on various coals. Only the proximate analyses of the coals were given, and it cannot be said that there was any real connection between the volatile matter and the oil or residue yield beyond the statement that those coals most easily converted had a volatile matter of over 40 percent. These papers [7] also described the large-scale continuous plant and indicated the yields and difficulties involved. The coal-oil paste plus about 5 percent of iron oxide and hydrogen were pumped into the first converter, which consisted of a horizontal steel cylinder closed at both ends by special joints and heated by gas through a lead-filled jacket. Three converters connected in series were used; each converter was equipped with a paddle stirrer. The contact time was about 2 hours. The yield

of oil was 40 to 45 percent, of residue 35 percent, and of gas 20 percent of the dry, ash-free coals. The products obtained in coal hydrogenation by the original Bergius process were of poor quality, high in oxygen, nitrogen, and sulfur compounds, and consisted chiefly of the less volatile high-molecular-weight hydrocarbons. Unfortunately no considerable increase in the yield of low-boiling hydrocarbons was brought about either by a change in working conditions or by hydrogenation of the liquefaction products. This is due to the fact that in the Bergius coal-hydrogenation process the hydrogenation velocity is too low to avoid polymerization of the primary products of the thermal dissociation of the coal. Even the highest applied hydrogen pressures proved insufficient except in the presence of suitable catalysts.[8]

The I. G. Farbenindustrie A.-G. succeeded in finding catalysts that greatly increased the velocity of the coal-hydrogenation reactions and started the development of coal hydrogenation in large-scale units in Germany in 1926. Ten years later 300,000 tons per year of motor fuel was being produced by the hydrogenation of brown coal and coal tar at the Leuna plant of the I. G. Farbenindustrie A.-G.; 100,000 tons per year from the hydrogenation of bituminous coal by the Hydrierwerke Scholven A.-G. at Gelsenkirchen in the Ruhr,[10] and 150,000 to 170,000 tons per year each from the hydrogenation of brown-coal tar by two plants operated by Braunkohle-Benzin A.-G., Brabag, one at Bohlen near Leipzig and the other at Magdeburg.[10] For 1938, German production of motor fuel from coal and coal tar by

[7] Bergius, F., *Z. Ver. deut. Ing.*, **69**, 1313–20, 1359–62 (1925) ; *Proc. 1st Intern. Conf. Bituminous Coal*, **1**, 102–28 (1926) ; *Can. Chem. Met.*, **10**, 275–9 (1926) ; *Petroleum Z.*, **22**, 1275–85 (1926).

[8] Grimm, H. G., *Proc. 3rd Intern. Conf. Bituminous Coal*, **2**, 49–65 (1931).

[9] Pier, M., *Génie civil*, **108**, 393–6 (1936), **109**, 7–11 (1936).

[10] Anon., *Gas World*, **104**, 421 (1936) ; *Z. österr. Ver. Gas- u. Wasserfach.*, **76**, 73 (1936).

hydrogenation was reported to have been about 1,500,000 tons.[11]

In Great Britain the Imperial Chemical Industries, Ltd., constructed a coal-hydrogenation plant at Billingham in England. This plant began operations in 1935 and has been producing about 150,000 tons of motor fuel per year from bituminous coal and coal tar by hydrogenation.[12] Experimental coal-hydrogenation plants have been in operation in England,[13] Japan,[14] France,[15] Canada,[16] and the United States.[17]

Coal-hydrogenation plants and procedures have been described in several publications,[18, 19, 20] but comparatively few important technical details have been disclosed.

Modern coal-hydrogenation processes, illustrated by the flow diagrams of Figs. 1 and 2, may be described briefly as follows. A mixture of about equal parts of powdered coal and heavy oil containing usually less than 0.1 percent of a catalyst such as iodine or stannous oxalate is pumped along with hydrogen at a pressure of 250 to 700

atmospheres through a preheater into the bottom of the liquid-phase converter. The term liquid phase is somewhat incorrect, for a considerable quantity of the hydrogenated coal vaporizes in the stream of hydrogen. It is used to differentiate the procedure from that of the vapor-phase stage, in which a fixed catalyst is used and practically all the (liquid) raw material is vaporized in a stream of hydrogen passing through the catalyst bed. The temperature may be raised to the liquid-phase working level of 400 to 480° C in the preheater, or additional heat may be supplied to the liquid-phase converters. Three converters are shown in Fig. 2 for the liquid phase. An industrial-size converter, about 4 feet inside diameter by 40 feet high, is illustrated by Fig. 3. The vaporized coal-hydrogenation products are carried by the excess hydrogen and the gaseous hydrocarbons formed in the reaction into a condenser, and subsequently the liquid product is separated from the gases in a condensate trap. The gases are scrubbed with oil under pressure to remove most of the hydrocarbons, and the resulting hydrogen is returned to the process.

The coal ash and unreacted coal particles are discharged suspended in a heavy oil consisting of hydrogenated coal that has not yet been sufficiently reduced in molecular weight to vaporize in the gas stream. The ratio of condensate to heavy oil is adjusted so that enough heavy oil will be recycled to be mixed with a fresh charge of coal. This ratio is controlled largely by regulation of the reaction temperature and the rate of coal-oil paste pumping, which is usually such as to give a contact time of about 2 hours based on the entire throughput. Obviously the vaporized hydrogenation products have a contact time much shorter than 2 hours, whereas the products

11 Anon., *Petrol. Times*, **42**, 641 (1939).

12 Gordon, K., *Gas J.*, **212**, 722–6 (1935); *Colliery Guardian*, **151**, 985–8 (1935). Anon., *Ind. Eng. Chem., News Ed.*, **17**, 438 (1939).

13 Booth, N., Williams, F. A., and King, J. G., *J. Inst. Fuel*, **11**, 42–9 (1937); *Dept. Sci. Ind Research (Brit.), Fuel Research Board, Tech. Paper* **44** (1938), 27 pp.

14 Leopold, H., *Ind. Eng. Chem., News Ed.*, **15**, 382 (1937).

15 Vallette, F., *Mém. soc. ing. civils France,* **90**, 740–5 (1937).

16 Warren, T. E., and Bowles, K. W., *Can. Dept. Mines and Resources, Bur. Mines Rept.* **798** (1940), 106 pp.

17 Storch, H. H., Hirst, L. L., Fisher, C. H., and Sprunk, G. C., *U. S. Bur. Mines, Tech. Paper* **622** (1941), 110 pp.

18 King, J. G., *Science of Petroleum*, Oxford University Press, London, Vol. 3, pp. 2149–52, 1938.

19 Gordon, K., *Trans. Inst. Mining Eng. (London)*, **82**, 348–59 (1931); *Proc. World Petroleum Congr. London*, **2**, 317–21 (1933); *J. Inst. Fuel*, **9**, 69–84 (1935).

20 Gordon, K., and Pier, M., *Chemistry & Industry*, **1933**, 284–8.
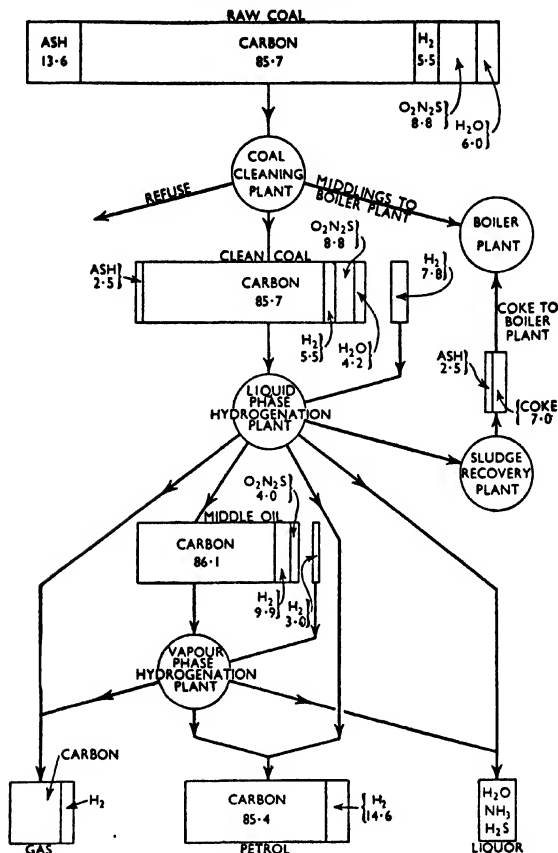
FIG. 1. Mass flow diagram for coal hydrogenation.[19]

appearing as heavy oils have a considerably longer contact time.

The crude condensate from the liquid phase is distilled and separated into three fractions, gasoline boiling up to 200° C, middle oil 200 to 300° C, and heavy oil boiling above 300° C. The heavy-oil slurry, or sludge, usually is centrifuged, and the wet solids are carbonized to recover heavy oil and a dry, solid residue. The heavy oil is recycled with the oil boiling above 300° C from the liquid phase, to be used in making a paste with powdered coal.

In the vapor-phase plant the liquid-phase middle-oil product boiling at 200 to 300° C is vaporized in a stream of 10 to 20 times its vapor volume of hydrogen, the mixture is preheated to 480 to 510° C (400 to 460° C for the more active catalysts), and passed through a bed of catalyst material. The pressure is in the range 250 to 700 atmospheres, and the catalyst usually
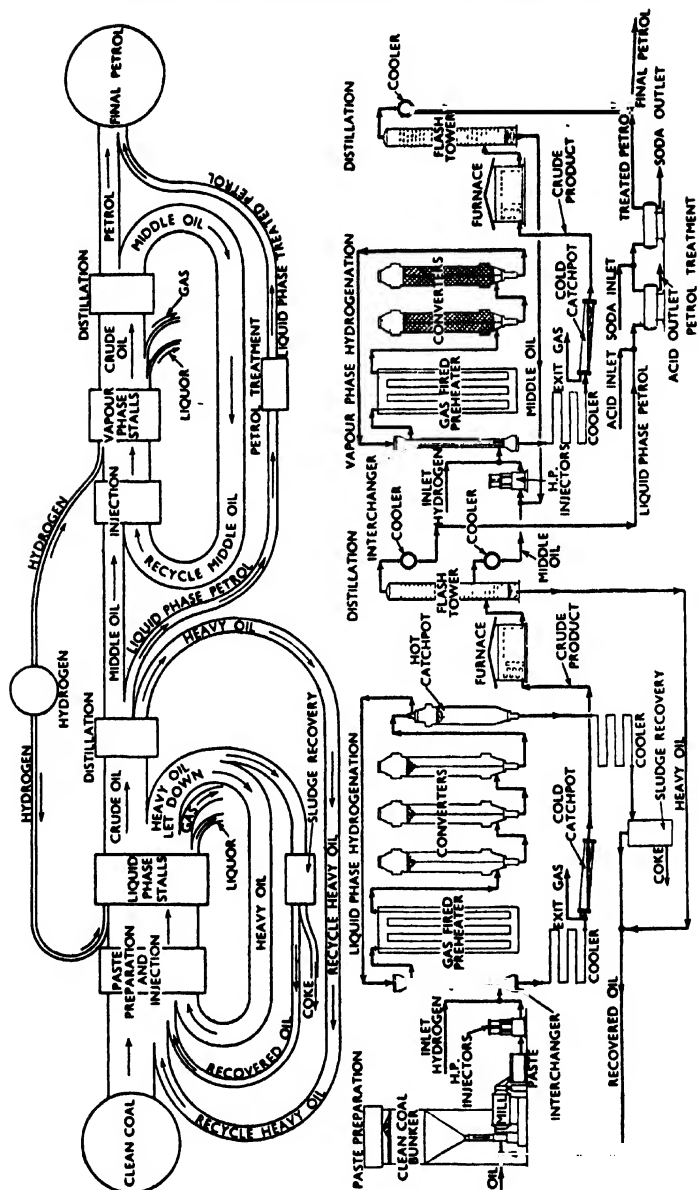
Fig. 2. Flow and line diagrams illustrating the liquid-phase and vapor-phase systems.[19]
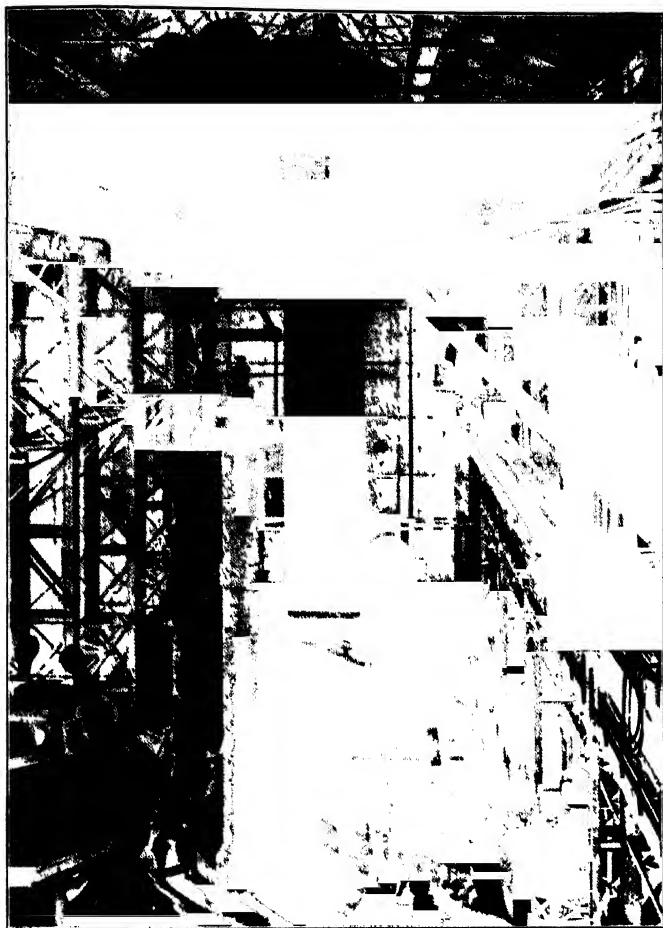
FIG 3. An industrial size coal hydrogenation converter.

contains 10 to 30 percent of molybdenum or tungsten sulfide and 70 to 90 percent of alumina, activated clay, or iron sulfide. The vapors leaving the converter are condensed, the oils passing to a distillation plant at atmospheric pressure, and the residual gas and surplus hydrogen to a gas-washing plant for hydrogen recovery. The throughput in the vapor phase is 1 to 2 volumes of liquid oil per volume of catalyst per hour. The liquid product is freed from water and distilled to give crude gasoline boiling to 200° C and an oil boiling above 200° C. The oil is recycled to the vapor-phase preheater.

A coal-hydrogenation plant of industrial

size is divided into a number of isolated units or "stalls," in which the converters, heat exchangers, and preheaters are arranged in one line on heavily piled founda-

Fig 4   A side view of coal hydrogenation stalls containing three converters and one preheater

tions   In each stall the converters, heat exchangers, and interconnecting piping, which are at high temperatures, are separated from the rest of the plant by the brick or concrete wall of the stall, which acts as a screen in the event of fire   The general arrangement of each stall may be seen in Figs 4 and 5

About 4 5 tons of coal is necessary to **produce 1 ton of gasoline,** this includes coal for the production of about 75,000 cubic feet of hydrogen and for all power and steam requirements   The overall thermal efficiency of the coal-hydrogenation process for gasoline production is about 42 percent [18]

IMPORTANT PHYSICAL-CHEMICAL FACTORS
IN COAL HYDROGENATION

Two excellent detailed reviews of the literature on the hydrogenation of coal and tar appeared in 1931 [21]   The important

[21] Skinner, D G , *Fuel,* **10,** 109–37 (1931)
Zerbe, C , *Chem Ztg* , **55,** 4, 18, 38, 94, 114, 136,
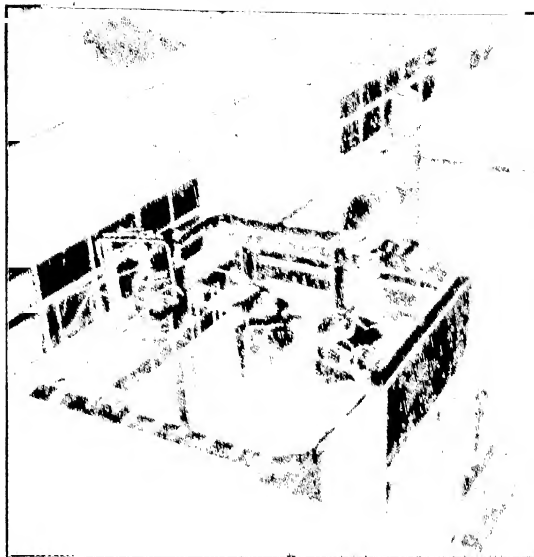
FIG. 5 A top view of a coal hydrogenation stall.

contributions made from 1931 to 1938 have been summarized briefly by Fieldner.[21] Two books by Berthelot and Hot [21] provide a comprehensive survey of the field of synthetic and substitute motor fuels, including coal hydrogenation and the synthesis of gasoline from purified water gas. The purpose of the present review is to present a critical discussion of the important physical and chemical factors involved in the liquefaction of coal by hydrogenation.

RANK AND TYPE OF COAL

The reactivity of coals to hydrogenation is, approximately, inversely proportional to their carbon content. In laboratory investigations using small bombs at 450° C about 100 atmospheres initial (cold) pressure of hydrogen, 2 hours at reaction temperature, and a number of British coals of different rank, the yield of distillable oils (boiling below 360° C at atmospheric pressure) was found to show an approximate linear relation to the carbon content of the coal.[22] More recent work on a large number of samples of the mechanically separable constituents of banded American coals, namely, anthraxylon (vitrain), spores, resins, fusains, attrital matter containing preponderant amounts of "opaque" attritus, and translucent attritus has been done under conditions similar to those under which work was done on the British coals.[23] The

162 (1931)   Fieldner, A C, *Minerals Yearbook, U S Bur. Mines,* **1933,** 433, **1934,** 627, **1935,** 691, **1936,** 625, **1937,** 935 , *U. S. Bur. Mines, Tech Paper* 613 (1940), 66–76   Berthelot, C, and Hot, A   *Carburants de synthèse et de remplacement,* Dunod, Paris, 1936, 350 pp ; *Technique et économie nouvelles des carburants de synthèse,* Dunod, Paris, 1937, 369 pp

22 *Dept Sci. Ind. Research,* (Brit.) *Fuel Research Board, Rept. for Year Ended March 31, 1936,* pp 152–60.

23 Fisher, C. H , Sprunk, G. C., Eisner, A., Clarke, L , and Storch, H. H., *Ind. Eng. Chem.,*

results show that those constituents of low- or intermediate-rank coals that are translucent in thin sections under the microscope are liquefied completely, that is, with little or no organic residue. The opaque constituents, namely, fusain and opaque attritus, contain, respectively, about 75 to 95 percent and 20 to 60 percent of materials resistant to hydrogenation. It is to be hoped that some fairly quantitative measure of the degree of opacity of "opaque" attrital matter and fusain will be developed; otherwise the petrography of a coal is at best only a semiquantitative index of its amenability to liquefaction by hydrogenation.

The coal constituents that are translucent in thin sections (5 to 10 microns thick) and that include spores, resins, oil algae, woody debris, and anthraxylon, usually contain less than 91 percent carbon and comprise the greater part of bituminous and lower-rank coals. The translucency of coal diminishes rapidly with increase in carbon content. All the constituents in coals containing more than about 91 percent carbon are so opaque that it is difficult to make sections thin enough to transmit light.

The products obtained by the hydrogenation of spores, resins, and oil algae are oils of low density that contain a high proportion of saturated hydrocarbons. Products obtained by the hydrogenation of anthraxylon, the principal constituent of most coals, apparently contain higher percentages of phenols and aromatic hydrocarbons.

The opaque coal constituents, which usually have carbon contents higher than 90 percent, are difficult to liquefy. Probably the opacity and difficulty of liquefaction of the opaque matter are directly proportional to its carbon content. Although the content of opaque constituents varies considerably and is high in some splint and cannel coals, the proportion of inert opaque matter in most coals in low. The liquefaction yield obtained by hydrogenation of materials high in opaque attritus varies over a wide range. Borderline material that is only slightly opaque but is nevertheless classified as opaque attritus by microscopic examination gives a liquefaction yield as high as 85 percent, whereas a yield as low as 40 percent is obtained from opaque attritus of a high degree of opacity.

The coal constituent that usually has the highest degree of opacity and the highest carbon content is fusain. This constituent, which resembles charcoal in appearance, is a mixture of a very opaque material (called "fusinite" by Seyler [24]) and 10 to 30 percent of translucent material. The fusinite is almost completely inert to hydrogenation, whereas the translucent material is partly, sometimes almost completely, liquefied by hydrogenation. The liquefaction yield obtained by hydrogenation of fusain depends primarily on the amount and nature of the translucent fraction and is usually between 5 and 25 percent.

Bright coals are relatively homogeneous mixtures of anthraxylon and translucent attritus, with usually less than 10 percent of total opaque matter. The above results, obtained by hydrogenation of the important mechanically separable coal constitu-

31, 190–5, 1155–61 (1939) ; *Fuel,* **18,** 132–41, 196–203 (1939), **19,** 182–8, 162–72 (1940). Wright, C. C., and Sprunk, G. C., *Penna. State Coll., Mineral Ind. Exp. Sta. Bull.* **26** (1939), 32 pp. **28** (1939), 23 pp. Fisher, C. H., Sprunk, G. C., Eisner, A., O'Donnell, H. J., Clarke, L., and Storch, H. H., *U. S. Bur. Mines, Tech. Paper* **642** (1942), 162 pp.

24 Seyler, C. A., *Proc. S. Wales Inst. Engrs.,* **53,** 254–327, 366–407 (1938) ; *Colliery Guardian,* **155,** 990–4, 1046–8, 1087–9, 1137–9 (1937).

ents, indicate that the behavior of bright coals upon hydrogenation should be directly proportional to their carbon content. For coals containing less than about 90 percent of carbon this expectation is found to be correct.[23]

Splint and cannel coals are highly heterogeneous, and hence the carbon content is only an average value that does not truly characterize the whole coal so far as chemical reactivity is concerned. Splint coals may be considered to be mixtures of constituents that, as judged by carbon content and opacity, differ enormously in rank. Splint coals generally give a poor liquefaction yield, and such yield is not simply related to the carbon content, as is true for bright coals.

Petrographic analysis is a desirable, although only semiquantitative, tool for the prediction of liquefaction yield upon hydrogenation. A very poor liquefaction yield predicted on the basis of petrographic analysis is, in general, reason enough for rejection of a coal as undesirable raw material for hydrogenation. A good prediction based on petrographic analysis or on high yield in small bomb tests does not exclude the possibility of severe engineering difficulties in continuous plant operation with a particular coal due to a number of factors that do not affect the operation of a small bomb but are of critical importance in continuous operation. Perhaps the most important of these critical variables is the optimum temperature range for the primary liquefaction of the coal. If this range is too narrow, the continuous plant may give markedly inferior results, because temperature control is not so precise as in the bomb tests. Another factor that makes it difficult to translate small bomb tests into the terms of a continuous plant is the viscosity of the coal-oil paste at pumping temperature and at

reaction temperature. A very marked specificity is attached to the peptization of the coal by the oil vehicle that carries it in suspension, and this determines the ease of paste pumping into the converter and the mechanical behavior (frothing, etc.) of the mixture of hydrogen and paste inside the converter.

Work done in the Bureau of Mines experimental plant on nine coals varying in rank from high-volatile bituminous to lignite showed fair agreement between petrographic estimates of organic residue yield and that obtained in continuous operation.[17] These data are given in Table I. The eighth and ninth columns show the organic residue yield predicted and measured, respectively. The last column shows that, except for the Mary Lee coal, there is a steady decrease, with decreasing rank, in the yield of oil per ton of coal as mined. The eleventh column shows that this decrease in oil yield with rank is much more gradual when it is calculated on a moisture-and ash-free basis.

PRETREATMENT OF COAL FOR HYDROGEN-ATION

In addition to the mechanical processes for crushing, washing, and grinding of coal before hydrogenation, the most important of the pretreatment processes concerns the neutralization of the basic constituents of the mineral matter in the coal. Hydrochloric, sulfuric, nitric, acetic, naphthalene sulfonic, formic, phosphoric, and other acids and acid salts are recommended by the patent literature as desirable additions to both bituminous and brown coals before hydrogenation.[25] It is interesting to

25 International Hydrogenation Patents Co., Ltd., Brit. Pats. 407,227, 408,002–4, 408,255 (1934), 422,892, 428,749 (1935) ; Fr. Pats. 780,-077, 780,826 (1935). I. G. Farbenindustrie A.-G., Brit. Pat. 432,489 (1935).

TABLE I

BUREAU OF MINES EXPERIMENTAL PLANT ASSAYS

(Percentages are by weight)

1	2	3	4	5	6	7	8	9	10	11	12	13
										Oil Yields		
Coal No.	State	County	Mine	Seam	Rank	Mois- ture in Coal as Mined	Organic Residue Pre- dicted	Organic Residue Ob- tained	Ash	Moisture and Ash-Free	Dry Coal	Coal as Mined
						%	%	%	%	%	%	%
1	Alabama	Jefferson	Sayreton	Mary Lee	Bit. H.V.A.	4.2	9.0	9.8	10.2	60	54	52
2	Pennsylvania	Allegheny	Bruceton	Pittsburgh	Bit. H.V.A.	1.6	7.8	4.0	5.7	70.5	65	64
3	Illinois	Franklin	Orient No. 2	Illinois No. 6	Bit. H.V.B.	7.8	5.4	4.9	7.1	70.5	65	60
4	Washington	King	Strain—Up- per Diamond	McKay	Bit. H.V.C.	9.6	0.5	1.1	4.1	68.5	66	59
5	Colorado	Weld	Puritan	Unnamed	Subbit. B.	24.1	8.0	5.6	5.4	63	60	45
6	Montana	Rosebud	Colstrip	Rosebud	Subbit. B.	25.1	8.2	6.7	10.1	60	55	40
7	Wyoming	Sheridan	Monarch No. 45	Monarch	Subbit. B	23.2	2.6	3.1	5.1	68.5	64	49
8	North Dakota	Mercer	Beulah, N. Dak.	Unnamed	Lignite	34.9	7.6	9.7	12.3	54.5	50	31
9	North Dakota	Ward	Velva, N. Dak.	Unnamed	Lignite	39.5	6.6	4.7	7.4	52	49	32

observe that except for about one year (in 1934–5) the subject of treatment of coal with acids before hydrogenation has not appeared in the patent literature. A Russian worker claimed that such additions of acids are harmful in hydrogenation of Ukrainian lignites.[26] It seems probable, in view of the rather short-lived interest in acid treatment, that a great many coals were soon found that did not react favorably in subsequent hydrogenation after additions of acid.

One patent has claimed that partial oxidation of coal by air at 120 to 350° C is a beneficial preliminary treatment.[27] Another patent advised oxidation by nitric oxide as desirable pretreatment for coals containing more than 84 percent carbon on a moisture- and ash-free basis.[28] Impregnation of the coal with sulfur or organic

sulfur compounds has also been recommended as pretreatment for hydrogenation.[29] Possibly sulfur impregnation is of value because of the catalytic activity of this element (see section on catalysts, pages 1763–72).

The heating of coal to 300 to 400° C in an inert atmosphere before hydrogenation serves to eliminate a considerable fraction of the oxygen as carbon dioxide and thereby raises the "available" hydrogen content of the coal. This procedure is particularly valuable for lignitic coals and peat where as much as 90 percent of the total oxygen in the dry coal can be eliminated as carbon dioxide.[30] The same objective is reached by treatment with aqueous caustic at 300 to 350° C.[31]

26 Makh, G. M., *J. Applied Chem. (U.S.S.R.)*, 12, 457–67 (1939).

27 Standard Oil Development Co., Fr. Pat. 703,731 (1930).

28 International Hydrogenation Patents Co., Ltd., Brit. Pat. 484,132 (1938).

29 International Hydrogenation Patents Co., Ltd., Brit. Pat. 459,268 (1937).

30 Warren, T. E., Bowles, K. W., and Gilmore, R. E., *Fuel*, 19, 72–6 (1940). International Hydrogenation Patents Co., Ltd., Fr. Pats. 792,-591, 793,834 (1936). Standard I. G. Co., U. S. Pat. 2,106,973 (1938).

31 Kasehagen, L., *Ind. Eng. Chem.*, 29, 600–4 (1937).

NATURE OF SOLVENT OR VEHICLE

Laboratory studies on the extraction of coal by various solvents indicate that depolymerization, followed by colloidal solution, occurs when an appreciable fraction of the coal is dissolved by solvents such as tetrahydronaphthalene or coal-tar fractions; and that organic liquids of high boiling point, medium dipole moment, and medium dielectric constant are the best solvents.[32]

Kiebler[33] has reported that the yields of extracts from a Pittsburgh Seam coal with 44 organic solvents can be very well correlated with the internal pressures of these solvents.

Most of the experiments[34, 35] on solvent extraction of coal under conditions comparable with those in coal-hydrogenation practice indicate that solution of the coal constituents, except ash, fusain, and some attrital matter, is rapid and complete.[35] In all these experiments, however, it is probable that, despite the absence of added catalysts and hydrogen gas, some hydrogenation occurred by transfer of hydrogen atoms from the solvent to the solute.

The data of Pott and Broche[35] showed that an optimum maximum temperature of extraction existed for each of the coals investigated. At temperatures higher than this optimum, reprecipitation of polymers occurred. The optimum temperature for most bituminous and brown coals was between 390 and 410° C when equal parts of coal and solvent (tetrahydronaphthalene : phenol : naphthalene = 2 : 1 : 2) were used. The product of this extraction resembled a primary coal tar. A procedure similar to that followed by Pott and Broche was patented in 1933 by Rose and Hill.[36] The use of the distillation residue from filtered Pott-Broche extract directly as a motor fuel or as raw material for coal hydrogenation has been the subject of many patents.[37]

IMPORTANCE OF VEHICLE, AGITATION, AND CATALYST

One would expect that, in a heterogeneous reaction such as that between coal-oil paste and hydrogen, agitation would be of paramount importance. Unfortunately, the evidence on this point is both meager and confusing. In experiments at the Bureau of Mines coal-hydrogenation plant[38] and in those of the British Fuel Research

32 *Dept. Sci. Ind. Research (Brit.), Fuel Research Board, Rept. for Year Ended March 31, 1935*, pp. 129-30. Agde, G., and Hubertus, R., *Braunkohlenarch.*, No. 46, 3-30 (1936). Asbury, R. S., *Ind. Eng. Chem.*, 28, 687-90 (1936). Gillet, A. C., *Brennstoff-Chem.*, 17, 421-9 (1936). Fisher, C. H., and Eisner, A., *Ind. Eng. Chem.*, 29, 939-45 (1937). See also Chapter 19.

33 Kiebler, M. W., Jr., *Ind. Eng. Chem.*, 32, 1389-94 (1940).

34 Boomer, E. H., Saddington, A. W., and Edwards, J., *Can. J. Research*, 12, 825-39 (1935), 13B, 11-27, 331-6 (1935).

35 Pott, A., Broche, H., Nedelmann, H., Schmitz, H., and Scheer, W., *Glückauf*, 69, 903-12 (1933) ; *Fuel*, 13, 91-5, 125-8, 154-7 (1934). Pott, A., and Broche, H., Brit. Pat. 293,808 (1927) ; Fr. Pat. 841,201 (1939).

36 Rose, H. J., and Hill, W. H., U. S. Pats. 1,916,330, 1,925,025 (1933).

37 Pott, A., and Broche, H., Brit. Pat. 293,808 (1927) ; Ger. Pats. 632,631, 633,693 (1936), 663,497 (1938) ; U. S. Pats. 2,123,380 (1938). 2,147,753 (1939). Uhde, F., Fr. Pat. 800,920 (1936) ; Brit. Pat. 489,664 (1938). Gewerkschaft Mathias Stinnes, Fr. Pats. 797,264-5 (1936) ; Brit. Pats. 464,337 (1936), 460,383, 462,478, 464,337 (1937), 480,214, 480,644 (1938), 505,729 (1939). I. G. Farbenindustrie A.-G., Fr. Pats. 813,251 (1937), 824,744 (1938) ; Brit. Pats. 466,336 (1937), 481,108, 493,307, 493,508, 494,834 (1938) ; Ger. Pat. 663,542 (1938). International Hydrogenation Patents Co., Ltd., Brit. Pats. 470,072 (1937), 491,543 (1938) ; Fr. Pats. 823,961, 827,600, 831,385 (1938), 840,763 (1939). Pott, A., U. S. Pat. 2,141,615 (1938). Pfirrmann, T. W., U. S. Pat. 2,167,250 (1939). Cf. also Gillet, A. C., *Rev. universelle mines*, 14, 653-5 (1938) ; *Colliery Guardian*, 157, 384 (1938). Scheer, W., *Feuerungstech.*, 27, 225-30 (1939).

38 Hirst, L. L., and others, *Ind. Eng. Chem.*, 31, 869-77 (1939).

Laboratory [39] variations in rate of hydrogen flow by a factor of about 10 produced no appreciable variation in yield in a given time interval (about 2 hours). However, the results obtained by Morgan and Veryard [40] for coal and tar hydrogenation under conditions such that turbulent flow of the reactants existed showed that the reaction rate was markedly increased by turbulence. This conclusion should be entertained with the reservation that, since Morgan and Veryard did not use a catalyst, the effect of turbulence may have been largely one of providing a catalyst, namely, the converter walls, by rupture of an adhering oil film on the metal surfaces.

Work by Storch, Fisher, Hawk, and Eisner [41] on the kinetics of hydrogen consumption, oxygen removal, and liquefaction in the hydrogenation of Pittsburgh Seam coal has shown that the rate of hydrogen consumption is limited by a diffusion process, presumably diffusion of the dissolved hydrogen through a liquid layer on the surface of the contact catalysts. This work was done in 1.2-liter rotating autoclaves, which involved no agitation by gas bubbling, and hence it is perhaps illogical to compare this system with that in a continuous plant. If, however, one assumes that neither the mechanical agitation in the rotating autoclave nor the agitation by gas bubbling in the continuous plant is capable of disturbing the liquid film on the catalyst surfaces, then relatively large changes in the amount of such agitation would not affect the rate of the contact

catalytic hydrogenation reaction, provided that no turbulence were produced. The advent of turbulence relative to the catalyst surface would produce a marked accelerating effect.

Concerning the effects produced in coal hydrogenation by adding a vehicle and catalysts to the coal, some experiments have been reported by Horton, King, and Williams,[42] some of whose results are given in Table II; and by Warren, Bowles, and Gilmore [43] in Table III.

TABLE II

SMALL AUTOCLAVE TESTS ON INFLUENCE OF VEHICLE AND CATALYST [42]

Experiment No.	Autoclave Contents			Oil Yield
	Coal	Vehicle *	Catalyst †	percent of coal
1	+ ‡	—	—	23
2	+	—	+	49
3	+	+	—	36
4	+	+	+	46
5	+	+	—	54.4
6	+	—	+	64.4
7	+	+	+	70.3

* Coal-tar distillate.

† 0.1 percent (on weight of coal) of SnO or GeO.

‡ Plus sign indicates presence of coal, vehicle, or catalyst; minus sign, absence of the constituent in question.

In experiments 1 to 4, inclusive, of Table II, the rotation of the converter and the presence of a loose metal rod served to agitate the contents. In experiments 5 to 7, inclusive, the converter itself was not rotated, but a mechanically driven stirrer was used for agitation. There were also other essential differences in procedure that make it illogical to compare the two groups. However, all comparisons made

[39] Booth, N., and Williams, F. A., *J. Inst. Fuel*, **11**, 493–502 (1938). *Dept. Sci. Ind. Research (Brit.), Fuel Research Board, Rept. for the Year Ended March, 1937*, p. 155; *ibid., for Year Ended March, 1938*, p. 208.

[40] Morgan, G. T., and Veryard, J. T., *J. Soc. Chem. Ind.*, **57**, 152–62 (1938).

[41] Storch, H. H., Fisher, C. H., Hawk, C. O., and Eisner, A., *U. S. Bur. Mines, Tech. Paper* **654** (1943), 49 pp.

[42] Horton, L., King, J. G., and Williams, F A., *J. Inst. Fuel*, **7**, 85–97 (1933).

[43] Warren, T. E., Bowles, K. W., and Gilmore R. E., *Ind. Eng. Chem.*, **11**, 415–9 (1939).

TABLE III

Yields of Volatile Products from Bituminous Coal with Stannous Oxide in the Presence and Absence of a Vehicle [43] *

(Percentage of dry, ash-free coal)

SnO as Percent of Charge	Without Vehicle		With Vehicle	
	Total	Increase Due to Catalyst	Total	Increase Due to Catalyst plus Vehicle
0.0096	63.8	9.0	72.7	14.2
0.0096	63.6	8.9	74.1	15.1
0.0951	68.9	14.6	79.4	20.2
0.0951	69.7	15.4	79.5	20.1
0.899	75.7	21.5	82.1	22.5
0.899	75.7	21.4	82.4	22.6
4.56	80.6	26.2	83.3	23.3
4.56	80.5	26.0	83.7	23.5
9.51	80.5	25.7	84.4	24 1
9.51	80.4	25.2	83.6	23.1

* Oil from hydrogenation of bituminous coal. Addition of vehicle alone resulted in 9.1 percent increase above the value (57.7 percent) for the coal without vehicle and without catalyst.

between experiments of the same group, that is, 1 to 4 or 5 to 7, are sound.

Comparisons of experiments 2 with 4 and 6 with 7 indicate an increase of 0 to 6 percent due to the addition of a vehicle when a catalyst is also present. Comparison of experiment 1 with 3 shows an increased yield of 13 percent due to the addition of a vehicle in the absence of a catalyst. Comparisons of experiments 3 with 4 and 5 with 7 indicate an increased yield of 10 to 16 percent due to the addition of a catalyst when a vehicle is also present. Comparisons of experiments 1 with 2, 1 with 3, 5 with 7, and 6 with 7 indicate that the addition of 0.1 percent stannous oxide as catalyst results in a greater increase in oil yield than the addition of the vehicle.

Inspection of Table III shows that the separate effects of catalyst and vehicle are not additive. With small amounts of catalyst the addition of a vehicle results in an appreciably enhanced yield; but with large amounts of catalyst, that is, more than about 0.5 percent, the effect is small and may even become negative. The two variables, catalyst and vehicle, are therefore not independent of each other; in fact, it is likely that catalysts such as those used for liquid-phase hydrogenation of coal increase the rate of production of liquid material from a portion of the coal; this liquid subsequently acts as a dispersion medium for the remaining solid material. Hence, if a larger proportion of catalyst is present, the production of a liquid vehicle is rapid enough to result in oil yields equal to or even greater than those obtained in the presence of both vehicle and catalyst.

This interpretation is also indicated by a more quantitative consideration of the data of Table III. In the absence of a vehicle the yield of volatile products is an approximately linear function of the logarithm of the percentage of stannous oxide used. This relationship holds until about 1 percent of stannous oxide is present; for larger percentages the increase in yield due to additional catalyst is smaller than would be expected. In the presence of a vehicle, however, the relationship between yield and amount of catalyst is such that the yield increases much more slowly than the logarithm of the percentage of catalyst used.

Catalysts. The catalytic behavior of the converter walls has been investigated by the British Fuel Research Laboratory [44] and found to be of considerable importance. These experiments were conducted in a 2-liter autoclave using a glass "liner"

44 *Dept. Sci. Ind. Research (Brit.), Fuel Research Board, Rept. for the Year Ended March, 1937,* pp. 149–51.

made of Pyrex. The results are given in Table IV.

Experiment 5 shows that Pyrex glass has very little effect, and, hence, conclusions concerning the catalytic effects of the converter walls and of the stannous hy-

TABLE IV

EXPERIMENTS ON WALL CATALYSIS WITH
2-LITER CONVERTER [44]

Beamshaw coal, low-temperature tar vehicle.
Contact time, 2 hours; temperature, 450° C.
Initial pressure, 100 atmospheres of hydrogen.

Experiment No.	Liner Fitted	Catalyst	Insoluble Residue percent of dry, ash-free coal
1	No	None	12.0
2	Yes	None	45.0
3	No	0.1 percent Sn(OH)₂	9.8
4	Yes	0.1 percent Sn(OH)₂	14.5
5	No	50 percent Pyrex glass	15.3

droxide are sound. In present industrial coal-hydrogenation practice the converters are about 4 feet in diameter, and, hence, catalysis by the converter walls may be of less importance than indicated in Table IV. It should be remembered, however, that in engineering development work such as was done by Vallette [15, 45] in France and by Morgan and Veryard [40] in Great Britain, where very much narrower tubes were employed than those in the experiments of Table IV, the catalytic effect of the converter walls is of considerable importance.

One might suppose that the activity of the converter walls would be decreased rapidly by poisoning. This supposition was disproved by experiments done in the British Fuel Research Laboratory.[46] The only

way in which converter-wall activity could be avoided was by the use of a glass liner. Indeed, one patent [47] specifies the periodic activation of the converter walls by the action of small amounts of iodine in the hydrogenation of pitch and coal. Iodine or its compounds is not added to the reaction mixture.

Additional data indicating the importance of the catalytic activity of the converter walls were reported in connection with some laboratory experiments on tar hydrogenation.[48] Three series of tests were conducted with two Irak tars: (1) in a bare autoclave of nickel-chromium-molybdenum steel without catalyst; (2) in the same autoclave lined with aluminum silicate; and (3) in the autoclave lined as in (2) but in the presence of a catalyst of molybdenum sulfide and tungsten. The results indicated that the walls of the autoclave had considerable influence on the hydrogenation process.

The nature of the catalysts employed in coal hydrogenation has been the subject of numerous patents. The presence of appreciable quantities of sulfur compounds and organic substances of high boiling points makes impractical the use of the well-known active hydrogenation catalysts such as reduced nickel. Moreover, such catalysts frequently show a negative temperature coefficient at temperatures of 400 to 500° C in hydrogenation reactions where sulfur and high-boiling organic substances are absent; because of this, they are not so active as other catalysts that are inferior to them at lower temperatures.[49]

The numerous patents disclosing catalysts for the destructive hydrogenation of

45 Vallette, F., *Bull. soc. encour. ind. natl.*, 135, 353–65 (1936).

46 Dept. Sci. Ind. Research (Brit.), *Fuel Research Board, Rept. for the Year Ended 1936*, p. 151.

47 Ges. für Teerverwertung m.b.H., Ger. Pat. 661,003 (1938).

48 Leopold, A., *Ann. combustibles liquides*, 14, 513–30 (1939).

49 Alchudzan, A. A., *J. Gen. Chem. (U.S.S.R.)*, 4, 1168–79 (1934).

coal and other carbonaceous materials may, for convenience, be classified in four groups as follows: (1) those emphasizing the desirability of the addition of some volatile halide or compound that will yield a volatile halide upon decomposition at process temperatures;[50] (2) promoted heavy metal sulfide and oxide catalysts;[51] (3) finely divided metals;[52] and (4) alkali and alkaline-earth metals and their compounds together with finely divided iron or other metals.[53]

This survey of the patent literature shows the outstanding importance of volatile halogens as catalysts in the primary liquefaction of coal by hydrogenation. This fact may be correlated with the abil-

ity of halogens, alkyl halides, and halogen acids to function as catalysts in the thermal decomposition of oxygenated organic compounds such as ethers and aldehydes.[54]

A few amphoteric sulfides—namely, molybdenum, and tungsten disulfides and stannous sulfide—are the most active of the metal sulfide catalysts. Stannous sulfide is reported to be particularly effective in the primary liquid-phase hydrogenation; molybdenum and tungsten disulfides are preferred for vapor-phase hydrogenation of tars or liquid primary coal-hydrogenation products. In general, the metal sulfides are more active than the oxides, and it is desirable to maintain a minimum partial pressure of about 1 atmosphere of hydrogen sulfide to avoid conversion of metal sulfides to oxides or to metals.[55] The work of Varga and Makray[56] showed that hydrogen sulfide used along with a molybdenum catalyst promoted the hydrogenation of naphthalene, m-cresol, and tar oils in general. Hydrogen selenide has a selective effect when used with a molybdenum catalyst, in that it promotes the hydrogenation of naphthalene more energetically than does hydrogen sulfide, and retards the hydrogenation of m-cresol and tar acids in general. The metalloids phosphorus, arsenic, selenium, and tellurium, or their compounds, are reported to be desirable additions to liquid-phase coal hydrogenation catalysts.[57]

[50] Holroyd, R., Cockram, C., and Imperial Chemical Ind., Ltd., Brit. Pat. 427,883 (1935). International Hydrogenation Patents Co., Ltd., Brit. Pats. 442,440, 450,473, 457,211 (1936); Fr. Pats. 779,872, 785,245, 787,520 (1935), 794,-437 (1936), 816,955 (1937). Mathews, M. A., Parsons, L. G. B., and Imperial Chemical Ind., Ltd., Brit. Pat. 440,456 (1935). I. G. Farbenindustrie A.-G., Ger. Pats. 654,024 (1937), 671,-183, 678,808 (1939); Brit. Pat. 472,538 (1937). Standard I. G. Co., U. S. Pat. 2,098,400 (1937).
[51] Yorkshire Tar Distillers Ltd., Brit. Pat. 435,192 (1935). I. G. Farbenindustrie A.-G., Ger. Pats. 614,910 (1935), 633,185 (1936), 657,-703, 658,651, 664,385, 666,065, 669,015 (1938), 670,717, 678,485, 678,622 (1939); U. S. Pats. 1,996,009, 2,005,192, 2,006,996 (1935), 2,039,259 (1936); Brit. Pats. 473,082 (1937), 488,651 (1938); Fr. Pat. 830,135 (1938). Deutsche Hydrierwerke A.-G., Ger. Pat. 611,922 (1935). Shell Development Co., U. S. Pat. 1,998,212 (1935). International Hydrogenation Patents Co., Brit. Pats. 442,573, 444,779, 455,313, 455,-453 (1936), 477,944 (1938); Fr. Pats. 793,436, 794,936 (1936), 814,334 (1937), 825,687 (1938). Standard I. G. Co., U. S. Pat. 2,159,511 (1939).
[52] International Hydrogenation Patents Co., Ltd., Brit. Pat. 442,440 (1936); Fr. Pats. 793,-464, 793,799, 794,437 (1936), 826,454 (1938). Standard Oil Company of Indiana, U. S. Pat. 2,033,737 (1936). M. Melamid, U. S. Pat. 2,110,-887 (1938).
[53] Comp. mines Vicoigne, Neoux, et Drocourt, Brit. Pat. 447,930 (1936); Fr. Pats. 787,211 (1935), 792,711 (1936). International Hydrogenation Patents Co., Ltd., Brit. Pat. 457,198 (1936); Fr. Pat. 793,108 (1936). Vieux, C., Brit. Pats. 442,023, 446,494 (1936).

[54] Glass, J., and Hinshelwood, C. N., J. Chem. Soc., 1929, 1815–9. Hinshelwood, C. N., Clusius, K., and Hadman, G., Proc. Roy. Soc. (London), 128A, 88–92 (1930).
[55] I. G. Farbenindustrie A.-G., Ger. Pat. 619,-739 (1935). International Hydrogenation Patents Co., Ltd., Brit. Pat. 452,915 (1936).
[56] Varga, J., and Makray, I. von, Brennstoff-Chem., 17, 81–3 (1936). Varga, J., Ger. Pat. 671,884 (1939). Fuchs, O., and Brendlein, H., Angew. Chem., 52, 49–58 (1939).
[57] I. G. Farbenindustrie A.-G., Ger. Pat. 677,-104 (1939).

British [58, 59] and Japanese [60] laboratory coal-hydrogenation investigations have included tests on various catalysts. The most interesting of the experiments made in the British Fuel Research Laboratory are those [59] on the effect of halogens when used alone and also in conjunction with stannous hydroxide and ammonium molybdate. Some of the results of these experiments on the hydrogenation of Beamshaw (bituminous) coal are given in Table V. With all the halogens except bromine

to the results achieved with either alone. Addition of hydrogen chloride gave the lowest yield of insoluble matter, but addition of iodine gave the best yield of distillable oils and the highest hydrogen consumption. Figures obtained by the British investigators (but not recorded here) for higher percentages of the halogens used with 0.1 percent of stannous hydroxide do not show any appreciable improvement over the results given in Table IV. Although 0.5 percent of ammonium molyb-

TABLE V

Experiments on the Effect of Halogens at 450° C [59]

Equal parts of Beamshaw coal and coal-hydrogenation heavy oil in 2-liter rotating autoclave; maximum pressure about 200 atmospheres; reaction time, 30 minutes; all figures in percentage of dry, ash-free coal.

Catalyst		Insoluble Residue	Oil Distilling below 310° C	Hydrogen Consumed
Nature	Percent			
None	....	23.2	12.5	0.5
Stannous hydroxide	0.1	8.2	22.0	3.1
Iodine	0.1	12.1	31.4	3.4
Stannous hydroxide	0.1 ⎱	8.2	38.2	4.6
Iodine	0.1 ⎰			
Bromine	0.1	7.7	31.4	3.9
Stannous hydroxide	0.1 ⎱	8.1	30.6	4.5
Bromine	0.1 ⎰			
Hydrogen chloride	0.09	12.5	27.5	2.7
Stannous hydroxide	0.1 ⎱	6.5	31.3	4.0
Hydrogen chloride	0.06 ⎰			
Ammonium molybdate	0.5	16.1	19.1	3.5
Ammonium molybdate	0.5 ⎱	7.8	33.4	3.9
Iodine	0.1 ⎰			

the result obtained with the halogen and stannous hydroxide together was superior

58 *Dept. Sci. Ind. Research (Brit.), Fuel Research Board, Tech. Paper 29* (1931), 37 pp., **42** (1935), 58 pp.

59 *Dept. Sci. Ind. Research (Brit.), Fuel Research Board, Rept. for the Year Ended March, 1938,* pp. 206–7.

60 Abe, R., Huzikawa, S., Kakutani, T., Okamura, T., and Sugiyama, K., *J. Soc. Chem. Ind. Japan,* **41,** Suppl. Bind., 417–21B (1938). Kurokawa, S., Hirota, K., Huziwara, M., and Asaoka, N., *J. Fuel Soc. Japan,* **18,** 32–6A (1939).

date is a poorer catalyst than 0.1 percent stannous hydroxide, a mixture of the former with 0.1 percent iodine is almost as good as the mixture of 0.1 percent stannous hydroxide with 0.1 percent iodine.

The Japanese investigators used 0.5- to 1-liter autoclaves, 430 to 450° C, 100 atmospheres initial (cold) pressure, and 1 hour reaction time. The halides, particularly chlorides and iodides, were found [60]

to be very active catalysts for coal hydrogenation. Of the metal oxides, both stannic oxide and nickel sesquioxide showed relatively high activity, molybdenum trioxide was fairly active, and ferric oxide displayed only a small catalytic influence. Stannic sulfide possessed marked activity, the sulfides of lead, copper, and nickel only small, and ferrous and manganous sulfides practically no catalytic influence. Among the metal chlorides, stannous and lead chlorides were very good catalysts; zinc, aluminum, bismuth, and ammonium chlorides were fair; and cuprous chloride, ferric chloride, and the chlorides of manganese, calcium, and barium were poor catalysts.

The results obtained from experiments with various catalysts for the liquid-phase hydrogenation of tar are in general very similar to those for liquid-phase coal hydrogenation. An extensive survey [61] was made in the British Fuel Research Laboratory, using for each experiment 250 grams of topped low-temperature tar, a 2-liter rotating autoclave, 100 atmospheres initial (cold) hydrogen pressure, 450° C, 2 hours reaction time, and 5 percent of powdered catalyst. The halogens were found to have outstandingly high catalytic activity, iodine being more active than bromine or chlorine. The hydrogen halides and volatile organic halides gave results similar to those of the halogens. Stannic oxide was a good catalyst, but stannous chloride was much superior. The power that sulfur possesses of activating other substances, or, it may be, itself acting catalytically in the presence of other substances, was found to be most marked with molybdic acid. Thus, whereas 2.5 percent of molybdic acid gave a tarry product containing 23.4 percent of pitch, a mixture of 2.5 percent each of

sulfur and molybdic acid yielded a light amber-colored oil, which was completely soluble in petroleum ether and which contained only traces of tar acids and bases. The effect of sulfur was also very marked when used with tungstic oxide. Tungstic oxide is, *per se*, inactive, but a mixture with an equal part of sulfur was an active catalyst. Iron, nickel, cobalt, and chromium oxides, which were only slightly active, showed some improvement when mixed with sulfur; but cadmium, tin, and vanadium oxides, which are mildly active catalysts, showed no improvement.

Most of the published information on catalysts for vapor-phase hydrogenation concern low-temperature tar rather than oils obtained from coal by hydrogenation. A considerable amount of experimental work published in England [61, 62] and Japan [63] on the hydrogenation of low-temperature tar showed that molybdenum oxide supported on alumina gel was a satisfactory vapor-phase catalyst when used at temperatures of 480 to 500° C and 200 to 300 atmospheres of hydrogen. It deteriorated at a relatively slow rate and could be reactivated by oxidation with air. However, for partly hydrogenated middle oils that are free from asphaltic and bitumenlike materials, much more active catalysts, such as pelleted molybdenum and tungsten disulfides, may be used. These catalysts may be prepared by precipitation of the sulfide by acidification of an ammonium thiomolybdate (or thiotungstate) solution followed by washing, drying, and pelleting of the powdered trisulfide and subsequent reduction to the disulfide. They are ex-

[61] Dept. Sci. Ind. Research (Brit.), Fuel Research Board, Tech. Paper 40 (1935), 107 pp.

[62] King, J. G., Science of Petroleum, Oxford University Press, London, Vol. 3, pp. 2156–61 (1938). Dept. Sci. Ind. Research (Brit.), Fuel Research Board, Repts. for Years Ended March, 1936, and March, 1937.

[63] Ando, S., J. Soc. Chem. Ind., Japan, 39, 278–80B (1936).

traordinarily active for vapor-phase hydrogenation, some hydrogenation being effected by them at as low a temperature as 250° C, although 380 to 400° C is the practical operating temperature.[62]

In 1933 Pier [64] provided some interesting discussion concerning the development of the vapor-phase sulfide catalysts. In semicommercial-scale tests molybdenum oxide catalysts were found to operate best at 450 to 480° C, and at 450° C they possessed a long life. It was, however, found necessary in full-scale production at Leuna to increase the temperature gradually in order to maintain the yield. At the higher temperatures the recycle oils were less saturated, and the gasoline product from operation at 500 to 530° C was more aromatic and of higher octane number than that obtained at 450° C. Later it was found that oxygen-free sulfide catalysts were about five times as active at 400 to 430° C as the earlier catalysts were at 450 to 480° C. Thus for example the new catalysts hydrogenated bituminous-coal-tar middle oil as readily as gas oil was hydrogenated by the old catalysts. However, the octane number was lower than that of the gasoline from the older catalysts, and further research was essential to discover catalysts of activity as high as that of the sulfide catalysts which would be of milder hydrogenating power, so as to avoid saturating the aromatic hydrocarbons. In 1938 a fairly complete disclosure was made of the results of this research.[65] It was found that dilution of the molybdenum or tungsten disulfide with 3 to 9 parts of ferrous sulfide, manganous sulfide, or activated clay yielded catalysts that, in addition to being much more active and rugged than catalysts like molybdic acid on alumina, were only mildly hydrogenating and gave a highly aromatic product.

Perhaps the most interesting part of this disclosure [65] concerns the specificity of the new catalysts for the production of aromatic hydrocarbons. Thus, for example, in the hydrogenation of crude cresol the catalyst was prepared by mixing 85 parts of ferrous sulfide with 15 parts of tungsten disulfide and pelleting the mixture. The product obtained at 450° C and 200 atmospheres pressure was 99 percent neutral oil containing 66 percent aromatics, chiefly toluene. With pelleted tungsten disulfide alone the product contained 3 percent of aromatics; with pelleted ferrous sulfide alone, 27 percent; with a pelleted mixture of 85 percent tungsten disulfide plus 15 percent ferrous sulfide the product contained only 5 percent of aromatics. Since, in all experiments, 98 to 100 percent neutral oil was obtained, it is apparent that there is a definite specificity attached to the 15 percent tungsten disulfide catalyst which is not possessed by either ferrous or tungsten sulfides *per se*, or by a mixture in which the tungsten sulfide predominates.

The composition of the gasoline products obtained by the hydrogenation of middle oils (from coal hydrogenation) with pelleted molybdenum disulfide is characteristically different from that obtained with molybdenum oxide on alumina gel,[66] as shown in Table VI.

The enormous differences in the results obtained with these catalysts cannot be due entirely to the fact that one is initially molybdic oxide and the other the disulfide, for it is probable that the oxide catalyst is at least partly converted to sulfide during

64 Pier, M., *Proc. World Petroleum Congr.*, **2**, 336 (1933).

65 I. G. Farbenindustrie A.-G., Brit. Pat. 488,-651 (1938).

66 Dept. Sci. Ind. Research (Brit.), *Fuel Research Board, Rept. for Year Ended March, 1937*, pp. 118–20. Hall, C. C., and Cawley, C. M., *J. Soc. Chem. Ind.*, **56**, 303-8T (1937).

TABLE VI

GASOLINES PRODUCED FROM MIDDLE OILS BY
DIFFERENT VAPOR-BASED CATALYSTS [66]

Percent by Weight	Alumina Gel-Supported Catalyst	Pelleted Catalyst
Aromatic hydrocarbons	27	2
Naphthenic hydrocarbons	66	50
Paraffinic hydrocarbons	7	48

operation. An X-ray study of the two catalysts probably would be profitable.

Some tests on various catalysts for the vapor-phase hydrogenation of coal-hydrogenation oils were reported by Makh in Russia.[67] The highest yield of gasoline was obtained with a mixture of about equal parts of molybdenum trisulfide and kaolin. A moderate yield of high-quality gasoline was obtained with a catalyst containing 10 percent of molybdenum disulfide or trioxide plus 90 percent zinc oxide-chromium oxide mixture.

As an example of the application of catalysts in coal hydrogenation, a rather exceptionally informative patent[68] discloses the following: In the first or liquid-phase stage the coal is mixed with an equal quantity of a heavy oil (obtained from the hydrogenation of the coal itself) and 0.06 percent tin oxalate plus 0.75 percent of hydrochloric acid. This mixture is pumped along with hydrogen at 400 atmospheres pressure through a preheater, where the temperature is raised to 450° C, and then through three converters in series. The function of the converters is to provide "soaking" space during the 2-hour time of contact. In the second or vapor-phase stage, that fraction of the filtered product distilling between 250 and 350° C is mixed with hydrogen at 300 atmospheres pressure and conducted at 350 to 400° C over a fixed tungsten disulfide catalyst. The time of contact for the vapor in this stage is about 1 minute, and the product is virtually free from oxygen, nitrogen, and sulfur. It is then passed along with hydrogen at 370° C and atmospheric pressure over a catalyst consisting of a mixture of molybdenum and cobalt sulfides deposited on active charcoal. This step removes the last traces of oxygen, nitrogen, and sulfur and adds hydrogen to some of the unsaturated hydrocarbons. The product is then cooled and the wax that separates is filtered off. In the last stage the filtrate of the third stage is subjected to destructive hydrogenation at 530° C with a catalyst consisting of a mixture of molybdenum, zinc, and magnesium oxides. The final product consists mainly of aromatic hydrocarbons such as benzene, toluene, and xylene.

Tropsch has presented some interesting data[69] on the action of catalysts in the hydrogenation of technical cresol (boiling range 86 percent between 185 and 200° C), gas oil, and paraffin wax at 370 to 460° C and 85 atmospheres initial (cold) pressure of hydrogen. Excellent catalysts for the high-pressure reduction of cresol were molybdenum, tungsten, and cobalt sulfides. Molybdic oxide was a very good catalyst; tungstic oxide was totally ineffective. Nickel hydroxide was a good catalyst, but nickel sulfide was of only moderate activity. Other moderately active catalysts were zinc chloride, aluminum hydroxide, vanadium oxide, chromium hydroxide, uranium oxide, and cobalt hydroxide; the following were without catalytic effect: zinc oxide, ferric hydroxide, and ferrous

[67] Makh, G. M., *Khim. T'verdogo Topliva*, 9, 58–64 (1938); *Chem. Abs.*, 32, 6429 (1938).

[68] I. G. Farbenindustrie A.-G., Brit. Pat. 472,-538 (1937).

[69] Tropsch, H., *Proc. 3rd Intern. Conf. Bituminous Coal*, 2, 35–49 (1931).

sulfide. A hydrogenation of the hydrocarbons formed occurred along with the reduction of the hydroxyl group, this hydrogenation being more extensive at lower than at higher temperatures. The cleavage of the methyl group from the cresol, amounting to only about 10 percent, was not influenced by the catalysts used.

Tropsch [69] found that the destructive hydrogenation of gas oil was catalyzed only by the sulfides of molybdenum and tungsten and, in some measure, also by the sulfides of the iron group. The oxides, on the other hand, were virtually ineffective; especially inactive was molybdic oxide, which served as an excellent catalyst for the reduction of cresols. Molybdic sulfide was an excellent catalyst for the destructive hydrogenation of paraffin wax. It appears, therefore, that whereas molybdic sulfide serves as catalyst for both C—C rupture and for hydrogenation, molybdic oxide does not catalyze the former reaction.

The experiments of Hollings, Bruce, and Griffith [70] on the influence of silica as a promoter for molybdic acid in the hydrogenation of tars showed that, when the yield under a given set of conditions was plotted against the atom percentage of silicon, a curve was obtained containing two maxima at 3.0 and 5.5 percent and a minimum at 4.5 percent. These authors also studied the adsorption, at temperatures up to 450° C, of hydrogen, benzene, hexane, and cyclohexane by molybdic acid containing varying amounts of silica. Inspection of the data given for the rate of activated adsorption of hydrogen shows that large decreases in the energy of activation occur between 0.0 and 3.0 atom percent silicon and between 4.4 and 5.5 percent, whereas this energy is virtually constant between 3.0 and 4.4 percent. If one assumes a steadily increasing retardation by coal tar or its hydrogenation products with increasing atom percentage of silicon, it is reasonable to predict on the basis of the changes in energy of activated adsorption of hydrogen precisely the form of curve actually obtained, that is, two maxima, one somewhere between 0.0 and 3.0 percent silicon and the other between 4.4 and 5.5 percent.

The efficiency of various promoters in increasing the catalytic activity of molybdenum oxide in the catalytic hydrogenation of phenol to benzene was studied by Kingman and Rideal.[71] It was found that a very effective method of introducing the promoter was to prepare the catalyst from the appropriate heteropoly acid, with the promoter as the central atom in the complex. The ammonium salts of the acids were used, and the catalysts were treated with hydrogen for 6 hours at 480° C before testing. Of the four catalysts prepared from $(NH_4)_n[X(Mo_2O_7)_6]$, where $X =$ phosphorus, silicon, tin, or thorium, those containing phosphorus and silicon were much more active than molybdenum oxide, whereas those containing tin and thorium were appreciably less active than molybdenum oxide. The three catalysts prepared from $(NH_4)_n[X(MoO_4)_6]$ containing nickel, chromium, and copper were much more active than molybdenum oxide.

X-ray analysis of the first group of catalysts showed an extremely small particle size for the phosphorus- and silicon-promoted catalysts, the structure of the catalysts containing phosphorus being entirely different from that of pure molybdenum dioxide. The thorium-promoted catalyst was more crystalline than that

70 Hollings, H., Bruce, R., and Griffith, R. H., Proc. Roy. Soc. (London), 148A, 186–206 (1935).

71 Dept. Sci. Ind Research (Brit.), Fuel Research Board, Rept. for the Year Ended 1936, pp. 142–44. Kingman, F. E. T., and Rideal, E. K., Nature, 137, 529 (1936).

promoted with phosphorus, and both the thorium- and the tin-promoted catalysts had structures similar to that of pure molybdenum dioxide. The efficiency of a promoter in the first group of catalysts may therefore be dependent on the prevention of the sintering of nearly amorphous catalysts. X-ray analysis of the second group showed a fairly well-developed crystalline structure similar to that of pure molybdenum dioxide, and hence the high activity of these catalysts may be due to an effect different from that for the phosphorus- and silicon-promoted catalysts of the first group. This effect may be the distortion of the space lattice caused by the introduction of the promoter. The relative surface areas of some of the catalysts were measured, and it was found that, though the more active catalysts presented larger areas, the variations in surface areas were not directly proportional to the measured differences in catalytic activity. Since, however, it is known that in heat sintering the activity of some catalysts decreases many times faster than the surface area, this lack of proportionality is not necessarily indicative of a new or qualitatively different phenomenon.

A detailed study of promoters for the dehydrogenation of hexane and the hydrogenation of phenol was published by Griffith.[72] The optimum promoter concentration for hexane decomposition at 500° C, with a molybdenum oxide catalyst, was found to be 4.3 atom percent for sodium, chromium, cerium, aluminum, barium, boron, and thorium, and 2.2 atom percent for iron, copper, and lead. The metal oxides of the first group were not reducible under the operating conditions, whereas iron, copper, and lead oxides were reduced to the respective metals. For the hydro-

genation of phenol at 400° C the optimum promoter concentrations for a molybdenum oxide catalyst were 16 atom percent for cerium, 16.5 for aluminum, and 15.0 for silicon. No adsorption measurements for phenol or hydrogen were reported, and until further data are available it will be difficult to determine the significance of these optimum promoter concentrations.

The same author also presented a series of experiments in which the rate was determined for dehydrogenation of decahydronaphthalene, decane, hexane, and cyclohexane, using chromic oxide gel plus various amounts of magnesia.[73] For decahydronaphthalene the activity was constant from 0.0 to 90.0 percent magnesia, and then it dropped off linearly with increasing magnesia content. For decane the constant activity ranged from 0.0 to 50.0 percent magnesia, for hexane 0.0 to 20.0 percent, and for cyclohexane the activity dropped continuously with increasing magnesia content. Griffith explained these data by assuming that the larger hydrocarbon molecules cover many active centers upon adsorption, and hence the dilution effect due to the inert carrier magnesia is not apparent until the active centers are farther apart than the necessary distance for activation and reaction. Similar experiments with a chromic oxide-silica catalyst and addition of various amounts of magnesia showed an immediate dilution effect with all hydrocarbons. Griffith concluded from this that chromic oxide promoted with silica presents a surface that is qualitatively different from unpromoted chromic oxide and not merely one with a larger number of active centers.

This research unquestionably will be of importance in developing the chemistry of

[72] Griffith, R. H., *Nature*, **137**, 538 (1936); *Trans. Faraday Soc.*, **33**, 407–12 (1937).

[73] Griffith, R. H., *Contact Catalysis*, Oxford University Press, London, 1936, pp. 88–89; *Trans. Faraday Soc.*, **33**, 412–6 (1937).

vapor-phase hydrogenation. It would be desirable, however, to have catalytic-rate studies on the destructive hydrogenation of larger molecules. There is also a dearth of rate measurements on destructive hydrogenation in the liquid phase of pure compounds of high molecular weight. Where relatively large molecules are involved, adsorption of such molecules will, beyond a certain limit, probably retard destructive hydrogenation reactions. Especially in liquid-phase hydrogenation of large molecules, the rate might be expected to be determined largely by that of the activated adsorption of hydrogen on a surface almost completely covered by the other reactant. It would, perhaps, be more logical to search for hydrogenation catalysts that do not strongly adsorb the organic molecule it is desired to hydrogenate destructively, or for hydrogenation catalysts that are soluble in the liquids to be hydrogenated, thus avoiding the necessity of a contact catalytic reaction. Tetrahydronaphthalene probably functions in part as a liquid-phase catalyst for coal hydrogenation, and very likely the desirability of compounds such as methylnaphthalene, phenols, and quinoline in liquid-phase coal hydrogenation systems may also be a matter of labile hydrogen atoms in these molecules in addition to their well-known solvent action on coal. Observations indicating that aromatic amines may be regarded as catalysts for the dehydrogenation of glyceraldehyde have been reported.[74]

TEMPERATURE, PRESSURE, AND CONTACT TIME

It is commonly supposed that one of the important reasons why a temperature above 400° C for the liquid phase of coal hydrogenation is necessary is the fact that active pyrolysis of coal does not occur until such temperatures are employed. This explanation is probably too simple, for other factors are involved, such as (1) the positive temperature coefficient of the solubility of hydrogen in most liquids, (2) the decrease in retardation of the reaction rate at high temperatures due to decreased adsorption of bituminous materials on the contact catalyst, and (3) the effect of temperature and particle size on the rate of depolymerization and solution of the coal substances.

Maxted and Moon[75] have shown that the temperature coefficient of the molar solubility of hydrogen in all the liquids tested by them is positive. With a given gas-liquid interfacial area, which is determined largely by the rate and manner of hydrogen recirculation, both the rate and the total equilibrium amount of hydrogen dissolved by a given weight of liquid increases with the temperature.

Körösy[76] plotted the critical temperature of gases against the logarithm of the molar solubility. He obtained a straight line for all solvents but found that hydrogen exhibits anomalous behavior in that its solubility is much higher than would be predicted from its critical temperature. Gases with critical temperatures above −93° C have negative temperature coefficients of solubility in liquids, and those with lower critical temperatures (such as hydrogen, helium, neon, nitrogen, carbon monoxide, argon, oxygen, and nitric oxide) have positive temperature coefficients in most solvents except water, which at about room temperature shows a negative coefficient for all gases. This is due to the fact that most solvents have appreciable expansion coefficients at room temperature,

[74] Strain, H. H., *J. Am. Chem. Soc.*, **60**, 1268 (1938).

[75] Maxted, E. B., and Moon, C. H., *Trans. Faraday Soc.*, **32**, 769–75 (1936).

[76] Körösy, F., *Trans. Faraday Soc.*, **33**, 416–25 (1937).

whereas that for water is very low. The temperature coefficient of solubility at constant volume of solution is negative for all gases and all solvents. Experiments made in the British Fuel Research Laboratory [77] also have shown that hydrogen has a positive temperature coefficient of solubility in hydrocarbon solvents and have yielded the results given in Table VII for the solubility

TABLE VII

SOLUBILITY OF HYDROGEN AND GASEOUS HYDROCARBONS IN TAR HYDROGENATION PRODUCTS [77]

Solvent	Hydrogenation Product of Low-Temperature Tar	Fraction of Product Boiling to 200° C	Fraction of Product Boiling from 200 to 300° C
Solubility at 20° C	Volumes of gas per unit volume of solvent per atmosphere partial pressure		
Hydrogen	0.065	0.090	0.050
Hydrocarbons	0.7	0.9	0 6

of hydrogen and a mixture of hydrocarbons (mainly methane plus ethane) in several oils. The temperature coefficient of the solubility of hydrogen in a middle oil is indicated by the data [78] of Table VIII.

TABLE VIII

TEMPERATURE COEFFICIENT OF HYDROGEN SOLUBILITY IN A MIDDLE OIL AT 200 ATMOSPHERES PRESSURE [78]

Temperature, °C	25	100	200	300	350
Hydrogen per kilogram of oil, liters	13	18	28	37	39

The heat of solution of the hydrogen calculated from these data ranges from about 9,500 calories for the 25 to 100° C interval to 16,000 calories for the 200 to 300° C interval. This variation may be due to failure to reach equilibrium.

[77] *Dept. Sci. Ind. Research (Brit.), Fuel Research Board, Rept. for the Year Ended March, 1935,* p. 102.

[78] Pier, M., *Proc. World Petroleum Congr.,* 2, 290–4 (1933).

Ipatieff and Levin [79] found that hydrogen is more soluble in alicyclic than in aromatic compounds, and the solubility in aromatic compounds · decreases with increase in the number of side chains. At low temperatures and pressures the solubility obeys Henry's law, but at higher pressures the solubility coefficient increases with increasing pressure.

Some data on the kinetics of the primary liquefaction of coal by hydrogenation have been obtained by H. H. Storch, C. H. Fisher, C. O. Hawk, and A. Eisner.[41] This work was done in a rotating 1.2-liter bomb with equal weights (100 grams of each) of tetralin and coal plus 1 percent of tin sulfide and an initial (cold) pressure of 1,000 pounds per square inch of hydrogen. The results indicate the following mechanism of the primary liquefaction of bituminous coal by hydrogenation:

1. The rate-determining step for the hydrogen absorption varies with temperature. Between 300 and 370° C, diffusion of hydrogen through a liquid film on the surface of the coal and catalyst is the slowest step; above 370° the rate-determining step is a chemical reaction between a hydroaromatic and the oxygen and unsaturated groups in the products of the primary decomposition of the coal. The chief function of the catalyst and of hydrogen at high pressure is to increase the rate of regeneration of a hydrogen carrier, which is a hydroaromatic compound such as tetrahydronaphthalene. The reactions of the hydrogen carrier with oxygen groups and double bonds are largely noncatalytic. The effects of the catalyst on the rate of oxygen elimination and on that of liquefaction are very similar, and it is probable that both processes are intimately

[79] Ipatieff, V. V., Jr., and Levin, M. I., *J. Phys. Chem. (U.S.S.R.),* 6, 632–9 (1935) ; *Chem. Abs.,* 29, 7718 (1935).

associated in one reaction or group of reactions.

2. There is no direct or simple relationship between the hydrogen-consumption rate and the rates of oxygen removal and of coal liquefaction. The most important factor in determining the rate of hydrogen consumption is the temperature, whereas almost complete liquefaction and extensive oxygen removal can be obtained at comparatively low temperatures and with relatively little utilization of hydrogen. The presence of a reservoir of reactive hydro-aromatic compounds that will transfer hydrogen to the products of the thermal decomposition of the coal substance is largely responsible for this apparent lack of direct dependence of the liquefaction and oxygen-removal rates on the rate of hydrogen consumption. For the maintenance of this reservoir of reactive hydroaromatics, active catalysts and high pressures of hydrogen are essential.

3. The data on the rate of hydrocarbon gas formation are in most respects similar to those for the hydrogen-consumption rate, except that there is little or no effect of the tin sulfide catalyst on the rate of the former process. The data for the rate of carbon dioxide formation are similar to those for the rates of coal liquefaction and oxygen removal. It is probable, therefore, that formation of carbon dioxide is coincident with the primary thermal decomposition of the coal substance.

4. The data on the rates of ammonia formation are markedly different from those for the rates of any of the other coal-hydrogenation reactions. The rates of ammonia formation during the first 2 hours are very slow and virtually the same for all temperatures. After the second hour, these rates increase rapidly for temperatures above 370° C and, up to removal of 25 percent of the total nitrogen, show no

tendency to decrease with increasing time. For all the other coal-hydrogenation reactions the rates increase very rapidly during the first hour and decline sharply at longer contact times. One possible explanation of the exceptional character of the ammonia-formation rates is that the nitrogen atoms are centrally located in the units of the coal structure, so that rupture of many carbon-to-carbon bonds precedes that of carbon-to-nitrogen bonds. A further indication of the extraordinary stability of the nitrogen group is the fact that the nitrogen contents of the pitch and the sulfur- and ash-free residue are about the same.

Morikawa [80, 81] and his associates have studied the effect of water vapor and of stannous chloride on the hydrogenation of coal in a 1-liter rotating autoclave. Their results indicate that the primary step of coal liquefaction occurs at temperatures of about 300° C and higher. This step is the production of bitumen upon fusion of the coal substance at about 340° C. It is accelerated by the presence of 5 to 20 percent of water and is profoundly affected by prolonged heating at low temperatures. The rate of production of normally gaseous hydrocarbons is but slightly affected by the presence of a catalyst such as stannous chloride, and Morikawa and his associates stated that the primary coal liquefaction reaction may be the change occurring inside the polymer molecules of the coal substance and have little to do with the side chains, which yield gaseous hydrocarbons upon hydrogenation. These authors believed that the primary reaction of coal liquefaction is the depolymerization of the coal substance, which involves some

80 Morikawa, K., Abe, R., Okamura, T., and Yamagata, K., *J. Soc. Chem. Ind. (Japan)*, **41**, Suppl. Bind., 431–4 (1938).
81 Morikawa, K., and Yamagata, K., *ibid*, **41**, 434–6 (1938).

hydrogenation and deoxygenation but little cracking (carbon-to-carbon normal valence bond rupture).

Tests were made at the British Fuel Research Laboratory [39] in a small-scale liquid-phase continuous plant of about 35 pounds of coal per day capacity on the effect of pressure, temperature, and contact time. Pressure variations were from 180 to 250 atmospheres; the effect was very small in this pressure range. The effect of increasing the paste input was to increase the heavy-oil product (boiling point above 310°) from zero at 1.2 pounds per hour to 22.9 percent at 2.2 pounds per hour. The temperature range studied was 420 to 460° C. The yield of insoluble residues was almost constant throughout, in contrast with the results of Hirst and his coworkers,[38] given in Table IX. The yield

TABLE IX

EFFECT OF TEMPERATURE ON HYDROGENATION OF PITTSBURGH SEAM COAL [38]

Contact time: 2 hours. Catalyst: 0.5 percent SnS + 0.5 percent MoO$_3$. Pressure: 200 atmospheres. All figures are in percentage of dry, ash-free coal.

Temperature, °C	Ash-Free Benzene-Insoluble Residue	Benzene-Soluble Oils	Normally Gaseous Hydrocarbons	Hydrogen Absorbed
420	16.3	73.0	10.4	5.8
433	11.3	71.0	20.7	6.1
447	7.2	67.0	35.2	7.7
459	6.3	57.0	39.8	7.8

of heavy oil decreased with temperature until it vanished at 460° C. Although some increase in gasoline (boiling point below 200° C) and middle oil (boiling point 200 to 310° C) accompanied this, there was also a large increase in gas formation.

The effect of temperature in the liquid-phase continuous hydrogenation of Pittsburgh Seam coal calculated from the re-

sults obtained by Hirst and his coworkers [38] is shown in Table IX.

The fraction of unreacted ash-free coal decreases markedly with temperature between 420 and 460° C, but the increased liquefaction does not result in an increased oil yield; the oil yield decreases, in fact, owing to a rapid increase in the amount of normally gaseous hydrocarbons produced. The effect of varying contact time, calculated from Hirst's data,[38] is shown in Table X. The increase in carbonaceous in-

TABLE X

EFFECT OF CONTACT TIME ON HYDROGENATION OF PITTSBURGH SEAM COAL [38]

Temperature: 440° C. Pressure: 200 atmosphere. Catalyst: 0.5 percent SnS + 0.5 percent MoO$_3$. All figures are in percentage of dry, ash-free coal.

Contact Time [*] hours	Ash-Free Benzene-Insoluble Residue	Benzene-Soluble Oils	Normally Gaseous Hydrocarbons	Hydrogen Absorbed
4.0	0.0	72.0	33.8	12.5
2.0	3.0	74.0	21.8	6.9
1.80	6.8	77.0	18.0	7.4
1.64	7.9	77.5	16.0	5.7
1.50	13.4	68.5	14.6	6.2

[*] This time is the number of hours required to pump one converter volume of paste. The heavy-oil slurry containing the unreacted coal was at reaction temperature for about 1.5 times the indicated contact time, owing to the continuous evaporation and removal of low-boiling products in the stream of hydrogen passing through the converter.

soluble residue and decrease in yield of gaseous hydrocarbons with decreasing contact time is accompanied by a slow increase in oil yield. The oil yield, however, reaches a maximum for contact times of about 1.6 hours and then decreases for shorter times. This maximum is due to the fact that for any given type of molecule solubility in benzene is determined largely by molecular weight. When the

contact time is too short to reduce the molecular weight below a certain limit, the oil yield, as measured by benzene solubility, must decrease. This explanation also accounts for the somewhat abrupt increase
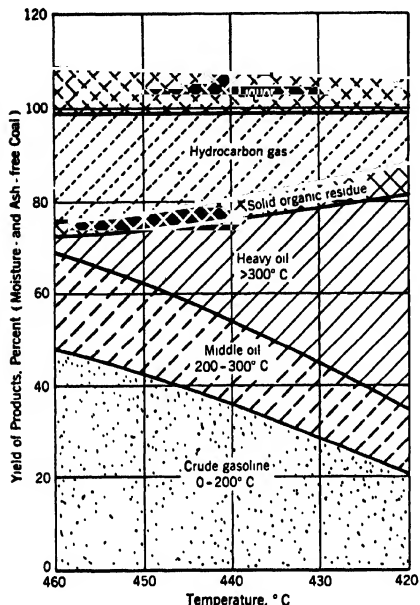
Fig. 6. Effect of temperature on yield of different products in liquid-phase hydrogenation of coal.[19]

in benzene insolubles for contact times less than about 1.6 hours.

The effects of temperature and contact time on the yield of the various products of coal hydrogenation are shown graphically in Figs. 6 and 7, respectively, constructed by Gordon.[19] The changes in yield of oil gas, organic solids, etc., are similar to those presented in Tables IX and X. In both sets of data the total yield is greater than 100 percent of the moisture- and ash-free coal, owing to hydrogen absorption.

The effects of temperature and contact

time are analogous, higher temperature being equivalent to a longer contact time. This equivalence applies even to the maximum in the oil yield as a function of contact time. Although Table IX does not indicate a maximum oil yield as a function of temperature it is very likely that such a maximum would be found at a temperature between 380 and 410° C. The last columns of Tables IX and X, presenting the hydrogen absorption as a function of temperature and contact time, respectively, show that the equivalence of these two variables for hydrogen absorption exists.

The markedly exothermic nature of the coal-hydrogenation reaction makes it necessary to have some means whereby the heat of reaction can be dissipated rapidly. In large coal-hydrogenation plants temperature control is facilitated by the introduction of a stream of cold hydrogen,[82] ammonia,[83] or other fluids [84] at several points in the converter systems for both liquid and vapor-phase hydrogenation.

Pressures of at least 200 atmospheres of hydrogen are found to be desirable in liquid-phase hydrogenation of coal at temperatures of about 450° C. At appreciably lower pressures, repolymerization occurs and coke is formed. The work of Pott and Broche [35] showed that 80 to 90 percent of the carbonaceous material in bituminous and subbituminous coals is rapidly dissolved by Tetralin-phenol mixtures at 390 to 410° C under the pressure created by

82 International Hydrogenation Patents Co., Ltd., Fr. Pats. 812,160, 817,287 (1937) ; Brit. Pat. 486,492 (1938).

83 I. G. Farbenindustrie A.-G., Ger. Pat. 633,-826 (1936). International Hydrogenation Patents Co., Ltd., Fr. Pat. 794,025 (1936) ; Brit. Pat. 444,936 (1936). Standard I. G. Co., U. S. Pat. 2,120,295 (1938).

84 International Hydrogenation Patents Co., Ltd., Fr. Pats. 827,024, 830,548 (1938) ; Brit. Pat. 497,382 (1938).
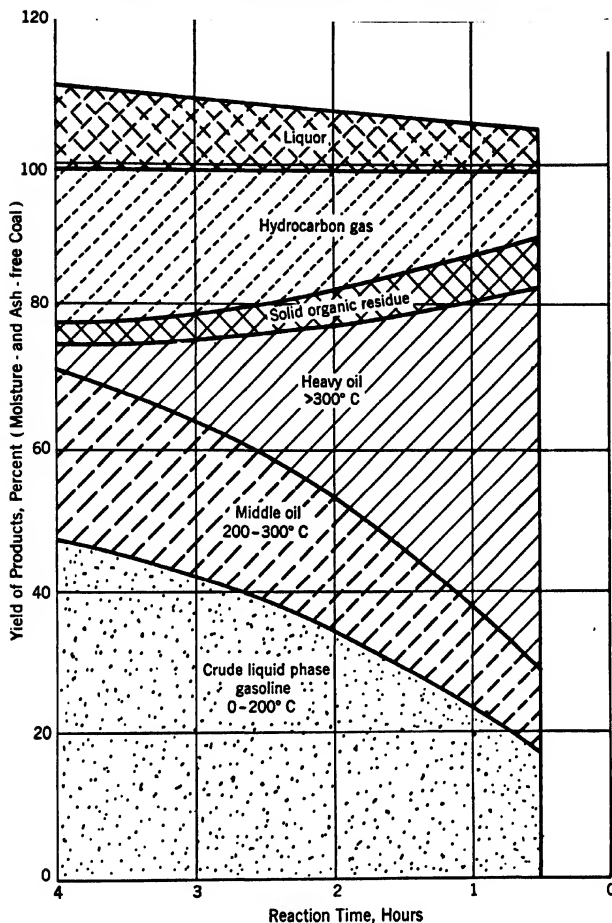
FIG. 7. Effect of contact time on yield of different products in liquid-phase hydrogenation of coal.[19]

the reaction mixture, i.e., with no added hydrogen.

The equilibrium partial pressure of hydrogen for the tetrahydronaphthalene-naphthalene equilibrium at 450° C has been reported to be about 10 atmospheres.[85] Hence it is thermodynamically probable

that hydrogen pressures greater than 10 atmospheres are not necessary for the primary liquefaction of coal. Two other possible functions of high-pressure hydrogen are: (1) to increase the amount of dissolved hydrogen, and (2) to accelerate the regeneration of hydroaromatic compounds such as tetrahydronaphthalene which serve as hydrogen carriers. It is probable that in

85 Maillard, A., *Ann. combustibles liquides*, 9, 1013–70 (1934).

liquid-phase coal hydrogenation the saturation of the unsaturated molecules produced by the thermal decomposition of the coal is accomplished mainly by reaction with hydroaromatic compounds and' to only a very minor extent by reaction with dissolved or catalytically adsorbed hydrogen. Hence the chief function of high hydrogen pressures and catalysts is probably the rapid regeneration of hydroaromatic compounds. The slow step in such regeneration may be the diffusion of one or both reactants to the catalyst surface.

As an example of the practical importance of high pressures in liquid-phase coal hydrogenation Pier [86] stated:

The conversion of old coals or of asphalts of high molecular weight, which goes but slowly at 200 to 300 atmospheres, proceeds without difficulty and at a satisfactory rate for large-scale production at considerably higher pressures, e.g., 700 atmospheres or more.

The results of experiments by King,[87] given in Table XI, show the effect of pres-

TABLE XI

EFFECT OF PRESSURE IN LIQUID-PHASE COAL HYDROGENATION [87]

Pressure		Products		
Initial atmospheres	Maximum atmospheres	Solids percent	Water percent	Oil percent
80	203	41.2	...	37.2
100	245	26.1	6.1	50.2
120	283	21.6	6.4	56.7

sure on the hydrogenation of Beamshaw coal at 445° C in the absence of a catalyst in small autoclaves.

In the vapor-phase destructive hydrogenation of oils obtained by hydrogenation of coal or coal tar in the liquid phase, high-pressure hydrogen is essential in order to

avoid condensation reactions leading to coke formation. It is not known, however, whether the necessity for high hydrogen pressures is of thermodynamic or of kinetic origin. Destructive hydrogenation reactions may be written and their equilibrium relationships calculated from specific heat data, which indicate that, thermodynamically, hydrogen pressures above 10 to 50 atmospheres are not necessary. Thus, for example, Sweeney and Voorhies [88] wrote the reactions:

$$C_{10}H_8 \; + \; 4H_2 \; = \; C_6H_6 + C_4H_{10}$$
naphthalene + hydrogen = benzene + butane

$$C_{14}H_{10} \; + \; 3H_2 \; = \; C_6H_6 + C_8H_{10}$$
anthracene + hydrogen = benzene + m-xylene
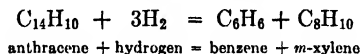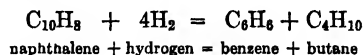
and calculated the equilibrium constant-temperature-pressure relationships from low-temperature specific-heat measurements. Their calculations showed that in the temperature range 450 to 480° C approximately 10 atmospheres pressure of hydrogen is sufficient to obtain a commercially satisfactory yield (about 50 percent conversion per pass), assuming that the reaction rates are large enough so that equilibrium may be reached in one pass at a reasonable space velocity. However, much higher hydrogen pressures, namely, 200 to 500 atmospheres, are found desirable in vapor-phase hydrogenation of oils. It is possible that much higher temperatures exist on the surfaces of the catalysts than in the gas phase, owing to the net exothermicity of the oil hydrogenation reactions, and at such higher temperatures correspondingly greater pressures of hydrogen are necessary for a satisfactory yield. It is more probable, however, that the desirability of 200 to 500 atmospheres of hydrogen is determined by reaction

86 Pier, M., *Trans. Faraday Soc.*, **35**, 967–79 (1939).

87 King, J. G., *J. Inst. Fuel*, **9**, 323–9 (1936).

88 Sweeney, W. J., and Voorhies, A., *Ind. Eng Chem.* **26**, 195–8 (1934).

rates at the catalyst surface rather than by thermodynamic relationships.

CHARACTERISTICS OF OILS PRODUCED IN LIQUID-PHASE HYDROGENATION OF COAL

Coal is usually hydrogenated for the single purpose of producing hydrocarbon fuels. Consequently, there has been little incentive to study the characteristics of intermediate products such as the "middle" oil (boiling range 210 to 330° C) from liquid-phase hydrogenation. As a source of organic chemicals, however, this intermediate product is most interesting and merits examination. The middle oils from liquid-phase coal hydrogenation contain benzene, toluene, xylene, cyclohexane, methylcyclohexane, about 20 percent of tar acids (phenol, cresols, xylenols), and 2 to 5 percent of nitrogen bases. On a unit basis these chemicals are more valuable than gasoline, and they are now produced and used in large quantities. Because of continued rapid expansion in the resin, lacquer, and solvent industries, larger amounts of many of these chemicals may be needed. It is indeed possible that, contrary to the situation in Europe, where in 1939 about 1,000,-000 tons of gasoline and Diesel fuel were produced by coal hydrogenation, the first commercial exploitation of this process in the United States will have for its main purpose the production of bulk organic chemicals such as phenol, cresols, xylenols, benzene, toluene, xylene, solvent naphtha, naphthalene, tetrahydronaphthalene, and pyridine bases. However, the oil products of liquid-phase coal hydrogenation cannot be properly evaluated as a source of organic chemicals and solvents until more is known about their composition.

Heyn and Dunkel [89] gave a detailed description of the oils obtained in the liquid-

89 Heyn, M., and Dunkel, M., *Brennstoff-Chem.*, 7, 20–5, 81–7, 245–50 (1926).

phase hydrogenation of a Lower Silesian coal. Unwashed coal dust containing 17.7 percent ash, 28.5 percent volatile matter, and an unusually high proportion of fusain was made into a paste with half its weight of an oil from a previous hydrogenation. This paste was hydrogenated in a continuously operating plant of about 15 pounds per hour capacity. The oil yield, which included 3.36 percent gasoline stripped from the gas, was 36.5 percent of the raw coal. The distribution of tar acids and bases is shown in Table XII. The total distillate

TABLE XII

DISTRIBUTION OF PHENOLS AND NITROGEN BASES IN A HYDROGENATED-COAL DISTILLATE [89]

Fraction	Pressure	Neutral Oil	Tar Acids	Tar Bases
°C	mm mercury	per-cent	per-cent	per-cent
To 180	760	80.7	18.0	1.3
180–220	760	61.2	34.2	4.6
To 150	15	81.4	14.1	4.5
150–190	15	89.4	6.1	4.4
190–230	15	90.7	3.2	2.9

contained 75.7 percent neutral oils, 12 percent tar acids, 3.5 percent bases, and small amounts of carboxylic acids, resin, and sediment.

The data of Table XII show that the lower tar acids (phenol, cresols, and xylenols) and the higher tar bases predominate. Phenol constituted 10.3 percent of the total tar acids; 66.5 percent of the total tar acids was the sum of the phenol plus cresols plus xylenols. The basic fraction contained several primary amines (aniline, toluidine, and xylidine) and unidentified secondary and tertiary nitrogen bases; collidine, quinoline, and quinaldine were identified. The gasoline condensed from the gaseous hydrogenation products contained benzene, toluene, xylene, and large quantities of their hexahydro deriva-

tives. The low-boiling fraction of the main product had an analogous composition. The fraction boiling at 180 to 220° C contained naphthalene and its tetrahydro and decahydro derivatives. A small amount of paraffin and considerable quantities of aromatics such as phenanthrene, carbazole, anthracene, and fluorene were obtained from the neutral oil.

By batch hydrogenation in small autoclaves of Maria Luisa long-flame coal, Pertierra [90] obtained an oil that contained 32 percent phenols and 8.2 percent nitrogen bases. The neutral oil boiling at 95 to 145° C contained 52 percent aromatic hydrocarbons (mainly benzene, toluene, and the xylenes), 28.7 percent saturates, and 7.3 percent unsaturates. The tar acids included phenol, pyrocatechol, and o- and m-cresol; the tar bases contained pyridine and 2,4-dimethylpyridine. Most of the bases were tertiary (68.6 percent), but 3.8 percent of primary and 27.6 percent of secondary bases were present.

The work of a number of British investigators shows that hydrogenation of Beamshaw,[91] Parkgate,[91] Lanarkshire,[92] and Mitchell Main [93] coals yields considerable quantities of tar acids, tar bases, and aromatic oils boiling from room temperature to 360° C. Similar results were reported for Japanese [94] and Canadian [16] coals.

An oil obtained by hydrogenation of a brown coal was described by Tropsch and Ter-Nedden.[95] This oil contained 22 percent tar acids and 3.5 percent nitrogen bases. Of the tar acids boiling to 280° C, 23, 11, and 14 percent, respectively, were phenol, o-cresol, and m-cresol.

Several patents mention the isolation of many polynuclear aromatic compounds of high molecular weight from coal-hydrogenation products. Sometimes the actual isolation is preceded by dehydrogenation. Products of this kind include pyrene,[96, 97, 98] chrysene,[96, 99] retene,[96] fluoranthene,[97] carbazole,[97] methyl- and dimethylpyrenes,[97] 1,12-benzoperylene,[97, 98, 100] coronene,[97, 98, 100] picene,[99] fluorene,[101] methylanthracene,[101] and naphthalene.[101]

The products of the hydrogenation of bituminous coals are largely aromatic and naphthenic in nature, whereas appreciable yields (about 12 percent) of the paraffin hydrocarbons have been reported in the hydrogenation of German brown coals.[102] The process for these coals begins with liquid-phase hydrogenation followed by a distillation of the primary liquefaction product. The light-oil fractions are subjected to vapor-phase hydrogenation to yield gasoline. Some of the middle oils are suitable (after removal of phenols) for Diesel fuel. The heavier fractions are used to provide raw material for lubricating-oil production and the pasting fluid for the lignite. Removal of asphalt, tar acids and

90 Pertierra, J. M., *Anales soc. españ. fís. quím.*, 28, 792–806 (1930), 30, 792–3 (1932).

91 Horton, L., Williams, F. A., and King, J. G., *Dept. Sci. Ind. Research (Brit.), Fuel Research Board, Tech. Paper 42* (1935), 58 pp.

92 *Dept. Sci. Ind. Research (Brit.), Fuel Research Board, Rept. for Year Ended March, 1930*, pp. 105–6.

93 Bakes, W. E., *Dept. Sci. Ind. Research (Brit.), Fuel Research Board, Tech. Paper 37* (1933), 214 pp.

94 Uchida, M., *J. Fuel Soc. Japan*, 14, 38–44 (1935).

95 Tropsch, H., and Ter-Nedden, W., *Brennstoff-Chem.*, 6, 143–5 (1925).

96 I. G. Farbenindustrie A.-G., Brit. Pat. 435,-254 (1935).

97 I. G. Farbenindustrie A.-G., Brit. Pat. 470,-338 (1936).

98 I. G. Farbenindustrie A.-G., Brit. Pat. 497,-089 (1937).

99 I. G. Farbenindustrie A.-G., Ger. Pat. 655,-103 (1938).

100 Scholl, R., and Meyer, K., *Ber.*, 71, 407 (1938).

101 I. G. Farbenindustrie A.-G., Ger. Pat. 659,-878 (1938).

102 International Hydrogenation Patents Co., Ltd., Brit. Pat. 450,721 (1936).

bases, and solid paraffins from the heavy oils results in an oil that is reported to be a fair lubricant. The asphaltic constituents are removed by vacuum distillation or solvent extraction, the asphalt being recirculated into the primary liquefaction stage. The asphalt-free heavy oil is then hydrogenated in liquid phase by means of special catalysts, and subsequently dewaxed. Table XIII gives the yield from two different

TABLE XIII

Yield of Gasoline, Lubricating Oil, and Paraffin Wax in Hydrogenation of Lignite [9]

	Lignite 1	Lignite 2
	percent	
Gasoline (60–66 octane)	33	37
Lubricating oil	13	13
Paraffin	11	7

lignites; the figures are percentages of ash- and moisture-free lignite, as presented by Pier.[9]

The lubricating oils obtained from lignite by hydrogenation may be of various grades. Their quality may be controlled by the choice of catalyst and the temperature and pressure of the final liquid-phase hydrogenation. The viscosity index of these oils is about 85, which is satisfactory for use in automobiles. The purity and melting point of the paraffin wax obtained by lignite hydrogenation are the same as those of paraffin wax from natural petroleum.

The products of the Bureau of Mines liquid-phase assay [17] of the coals listed in Table I contained about 20 percent boiling in the gasoline range and 70 percent distilling between 200 and 330° C. About 25 percent by volume of this oil was phenolic. The yield of tar acids as percentage of the dry, ash-free coal is given in Table XIV. The coals are the same as those of Table I.

The commercially important tar acids, those boiling below 235° C, contain about 50 percent xylenols, 40 percent cresols, and 10 percent phenol. It is estimated that upon recycling the tar acids boiling above 235° C, 25 percent would be converted into low-boiling tar acids and 75 percent into hydrocarbons. The highest yields of low-boiling tar acids were obtained from Pittsburgh Seam bituminous coal, Monarch No. 45 subbituminous, and Velva lignite.

Perhaps the most significant data to be correlated with rank are those given for the total yield of aromatic oil in the seventh column of Table XIV. With the exception of the Mary Lee Seam coal (No. 1) there is a steady decrease in yield of aromatics with increasing oxygen content of the coal (second column, Table XIV).

The third column of Table XIV shows that there is little, if any, trend with rank of coal observable in the hydrogen used per ton of coal. However, the hydrogen used per ton of oil produced (column 3, Table XIV, divided by column 11, Table I) increases from about 0.12 ton for bituminous coals to about 0.15 ton for lignites. This increase is much smaller than one might have predicted upon considering the oxygen contents (column 2, Table XIV) of the coals. This somewhat surprising result is apparently due to removal of most of the oxygen as carbon dioxide rather than as water, when the original oxygen content of the coal exceeds about 10 percent.[103]

The neutral oils obtained in the Bureau of Mines assays contained 40 to 70 percent of aromatics, about 10 percent of olefins, and 20 to 50 percent of saturates containing approximately equal parts of paraffins and naphthenes. The aromatic content of the neutral-oil fractions increased with in-

[103] Fisher, C. H., Sprunk, G. C., Eisner, A., Fein, M. L., Clarke, L., and Storch, H. H., *Fuel*, 19, 16–20 (1940).

TABLE XIV

BUREAU OF MINES EXPERIMENTAL PLANT ASSAYS, PERCENTAGE OF DRY, ASH-FREE COAL [17]

Coal No.	Oxygen Content of Coal	Hydrogen Used	Tar Acids		Tar Bases	Total Aromatics
			Distilling to 235° C	Distilling 235 to 330° C	Distilling to 330° C	
1	5.0	8.5	3.9	3.5	2.3	32.8
2	6.8	9.0	7.6	3.5	2.8	40.9
3	10.0	8.5	4.4	7.0	1.3	37.1
4	12.5	7.6	4.9	8.1	3.2	27.7
5	16.4	9.7	6.2	6.0	2.6	28.2
6	16.2	7.5	6.9	6.9	1.8	26.4
7	16.9	8.5	7.8	7.1	2.8	25.4
8	19.4	8.0	5.3	6.1	1.3	23.5
9	21.2	7.0	8.0	6.1	1.8	22.1

creased boiling point, and aromatic hydrocarbons predominated in all the fractions above 188° C. The 20 to 188° C neutral-oil fractions contained 18 to 36 percent aromatic and 55 to 71 percent saturated hydrocarbons.

The saturated oils remaining after several extractions with an excess of sulfuric acid had comparatively low refractive indexes, indicating the presence of considerable amounts of paraffin hydrocarbons. An estimate of the paraffinicity was made by comparing the refractive indexes and boiling points with those of typical pure compounds. The first fraction (20 to 188° C) contained, on the average, about 0.5 ring per molecule; therefore, this fraction contained about 50 percent paraffins. The higher fractions contained 0.8 or 0.9 ring per molecule, and the average molecules could be pictured as alkyl cyclohexanes. Probably the paraffins present are mainly of the branched-chain type. Because of the highly cyclic structure usually attributed to coal, it should be stated that the content of paraffins corresponds to about 10 percent of the dry, ash-free coals. For the higher fractions of saturated hydrocarbons, the production of cyclohexane de-

rivatives would require the rupture of two or three rings.

A sample of about 10 liters of assay oil from Pittsburgh coal [38] was separated into tar acids, tar bases, and neutral oil by extraction with sodium hydroxide and sulfuric acid solutions. Ether or benzene extraction was employed to remove tar bases and acids from the amine sulfate and sodium phenolate solutions, respectively. This separation yielded 17.3 percent tar acids and 5.8 percent tar bases by volume (19.0 and 6.2 percent by weight).

From the distillation curves for the neutral oil, tar acids, and tar bases it was estimated that about 35 percent of the tar acids was phenol and cresol and about 30 percent was xylenols. Distillation of the lower tar acids through a more efficient column showed that the phenol fraction, which solidified on standing at room temperature, amounted to about 8 percent of the total tar acids. The approximate composition of the tar acids is shown at the top of the next page.

Since most of the tar bases boiled above 190° C, pyridine and its methyl and dimethyl derivatives (picolines and lutidines) were present only in small quantities. Tar

	PERCENTAGE OF TOTAL TAR ACIDS
Phenol	8
Cresols	27
Xylenols	30
Higher phenols	35
	100

bases of high boiling point that might have been present are tri- and tetramethylpyridines, toluidine, indole and its alkyl derivatives, quinoline and its alkyl derivatives, isoquinoline, and naphthylamines.

The neutral oil boiling below 200° C was examined further to obtain an estimate of the benzene, toluene, xylenes, naphthenes, and paraffins present. The data shown in Table XV were obtained by distilling 787

17 inches. Olefins and aromatics were determined by extracting 5 cubic centimeters of oil successively with 85 and 98 percent sulfuric acid.

Large quantities of saturated hydrocarbons were in the neutral oil, especially in the lower fractions (Table XV). The aromatic hydrocarbon content increased with molecular weight or boiling point. The aromatic hydrocarbons in fractions 2 and 3 were principally benzene and toluene, respectively, and the data in Table XV can be used to estimate the amounts present. It is possible that some of the olefins removed by extraction with 85 percent sulfuric acid contained aromatic rings—styrene and indene, for example.

TABLE XV

NEUTRAL OIL BOILING BELOW 200° C FROM PITTSBURGH OVERHEAD OIL [104]

Boiling range, °C	20–70	70–100	100–125	125–150	150–175	175–200
Percent of neutral oil by volume	0.57	2.1	2.2	4.1	2.3	2.3
Refractive index of neutral oil at 20° C	1.4167	1.4224	1.4306	1.4478	1.4613	1.4831
Olefins, percent of fraction	....	9.0	6.5	5.5	4.0	3.0
Aromatic hydrocarbons, percent of fraction	....	15.5	20.5	32.5	39.5	53.0
Saturated hydrocarbons, percent of fraction	....	75.5	73.0	62.0	56.5	44.0
Saturated oil:						
refractive index of saturated hydrocarbons at 20° C	....	1.4145	1.4166	1.4235	1.4306	1.4361
Average number of rings per molecule *	....	0.9	0.7	0.7	0.6	0.7
Naphthenes, percent †	....	86	70	70	69	65
Paraffins, percent †	....	14	30	30	31	35

* Estimated from boiling point, refractive index curves of pure compounds.
† From boiling point, refractive index chart of McArdle and coworkers. See ref. 104.

cubic centimeters of neutral oil from the Pittsburgh assay oil through a column packed with glass helices over a length of

104 McArdle, E. H., Moore, J. C., Terrell, H. D., and Haines, E. C., *Ind. Eng. Chem., Anal. Ed.,* 11, 248–50 (1939).

The saturated hydrocarbons were isolated for further study by several extractions with an excess of 98 percent sulfuric acid. As judged by refractive indexes, all fractions of the saturated oil were predominantly naphthenic (Table XV). The

low-boiling saturated hydrocarbons from Washington and Colorado coals were about 50 percent naphthenic.

From the data obtained for the liquid-phase hydrogenation products of Pittsburgh Seam coal, the estimate of Table XVI was made of the composition of the

TABLE XVI

COMPOSITION OF LOW-BOILING NEUTRAL OIL FROM LIQUID-PHASE HYDROGENATION OF PITTSBURGH SEAM COAL

Constituent	Volume Percent of 20° to 210° C Fraction
Benzene	1.5
Toluene	2.1
Xylene	6.3
Cyclohexane and Methylcyclohexane	6.1
Dimethylcyclohexane	4.5
Tetrahydronaphthalene	13.9
Polyalkylbenzenes	65.6

neutral-oil fraction boiling in the 20 to 210° C range.

HYDROGENATION OF COAL TAR

Tar hydrogenation is a less cumbersome engineering task than coal hydrogenation, in that no solid materials other than a very small amount of catalyst powder must be introduced or removed from high-pressure vessels. In other respects the hydrogenation of tar presents the same problems as the hydrogenation of coal. Low-temperature tar may be processed directly in the vapor phase; that is, the tar, mixed with some recycle oil, and hydrogen are passed through a body of catalyst granules held fixed inside the high-pressure vessel. High-temperature tars, however, must be processed first in the liquid phase, in which a small amount of catalyst is mixed with the tar and the mixture pumped into the converter, and then the middle-oil product of the liquid phase is treated as described above for low-temperature tar.

The hydrogenation of low-temperature tar has been studied in Great Britain,[62, 105] Germany,[106] Japan,[107] and Russia.[108]

An experimental plant with a capacity of 1 to 2 tons (200 to 400 gallons) per day has been erected and operated at the British Fuel Research Station in Greenwich.[109] Low-temperature tar was mixed with an equal volume of recycle oil and pumped along with 200 to 500 cubic feet of hydrogen (measured at atmospheric pressure) per gallon of tar through a heat exchanger (reactants raised to 300° C) and preheater (to 400°), to the converter, where the reaction proceeded at 480° C and 200 atmospheres pressure. The 80° C difference between preheater and converter was maintained by the heat of reaction, which is about 360 Btu per pound or 200 calories per gram. The converter had a pressure retaining wall 3 inches thick, and was 16 inches in inside diameter and 13 feet long. This wall was separated from the reaction chamber by an annulus of kieselguhr, which

105 Cawley, C. M., and King, J. G., *Dept. Sci. Ind. Research* (Brit.), *Fuel Research Board, Tech. Papers* **41** (1935), 17 pp., **45** (1937), 45 pp., **48** (1938), 55 pp., **51** (1939), 36 pp.

106 Winter, H., Free, G., and Mönnig, H., *Oel u. Kohle*, **12**, 934-43 (1936). Rühl, G., *Bergbau*, **50**, 289-98, 303-9 (1937).

107 Ando, S., *J. Soc. Chem. Ind., Japan*, **37**, Suppl. Bind., 357-61 (1934), **38**, 145-8, 196-9, 267-9 (1935), **39**, 133-4, 278-80, 447-9 (1936), **40**, 12-4, 83-5, 124-5 (1937), **41**, 191-3, 215-7, 247-8, 292-5, 315-6, 386-91, 411-2 (1938), **42**, 27-9, 69-71, 147-50, 171-3, 213-5, 232-4, 268-71 (1939), **43**, 35-40 (1940). *J. Fuel Soc. Japan*, **16**, 21-30 (1937), **17**, 32-42 (1938).

108 Altman, L. S., Diner, I. S., Mitkalev, B. A., Nemtsov, M. S., and Ryskin, M. I., *Khim. Tverdogo Topliva*, **6**, 926-42 (1935), **7**, 31-48 (1936).

109 King, J. G., and Shaw, J. F., *Trans. Chem. Engr. Congr., World Power Conf.*, **3**, 463-99 (1936). Tupholme, C. H. S., *Ind. Eng. Chem. News Ed.*, **16**, 221 (1938). Cawley, C. M., and King, J. G., *Dept. Sci. Ind. Research* (Brit.), *Fuel Research Board, Tech. Paper* **51** (1939), 36 pp.

served to keep the pressure retaining wall cold. The reaction space or catalyst basket was 8 inches in diameter and 11 feet long. The catalyst consisted of ¼- to ⅛-inch particles of alumina gel impregnated with 25 percent of its weight of ammonium molybdate and subsequently heated in air at 500° C to drive off the ammonia. In use, the molybdic acid was converted to molybdenum disulfide by the hydrogen sulfide formed from the sulfur compounds in the tar. About 200 pounds of catalyst was required to fill the reaction chamber.

The overall yield of oils boiling in the gasoline range (20 to 200° C) was about 100 percent by volume and 72 percent by weight of the raw tar. These oils contained about 68 percent of saturated hydrocarbons (paraffins plus naphthenes), 30 percent of aromatic hydrocarbons, and 2 percent of olefins (see Table XXV). The hydrogen consumption was about 60 cubic feet per gallon of tar, or about 10 percent by weight of the tar. If the hydrocarbon gases formed were converted into hydrogen by reaction with steam, about 25 cubic feet of hydrogen would be generated per gallon of tar. It might, however, be more profitable to make hydrogen from coke-oven gas and sell the hydrocarbon gases produced in tar hydrogenation as fuel gas.

The catalyst slowly deteriorated, owing to the deposition of highly carbonaceous materials on its surface, until after about 30 days it was essential that it be regenerated. This was done by oxidation with air at 500° C until the initial activity was restored. This periodic life is equivalent to 300 volumes of tar per volume of catalyst, or 400 pounds of tar per pound of molybdenum disulfide.

The procedure used for vapor-phase hydrogenation of the middle oils from liquid-phase coal hydrogenation is virtually identical with that for low-temperature tar.

The yield of gasoline is about 100 volume percent and 70 percent by weight, and the composition of the gasoline is about the same as that given above for the product of low-temperature tar hydrogenation (see Table XXV). The significant differences in the composition of the liquid-phase coal-hydrogenation products from various coals are greatly reduced upon further hydrogenation of these middle oils to gasoline. The composition of the gasoline produced is largely determined by the catalyst (see Table VI) and temperature of the vapor-phase operation.[66] The introduction of two catalyst treatments in vapor-phase hydrogenation results in greater control of the chemical composition and physical properties of the product. For example,[110] a middle oil may be first hydrogenated by 40 to 80 seconds contact at 390 to 440° C with a powerful saturation and splitting catalyst, such as tungsten disulfide, to yield a mixture of gasoline and higher-boiling oil. This mixture is then treated at a higher temperature (450 to 600° C) over a dehydrogenating and splitting catalyst, such as an oxide of the sixth group of the periodic system (for example, chromium or molybdenum), mixed with zinc oxide to give a highly aromatic product, which is then blended with the gasoline fraction from the first treatment using tungsten disulfide as catalyst.

The effects of varying the pressure, temperature, contact time, and other important factors in vapor-phase hydrogenation of low-temperature tar have been summarized by King[62] and by Cawley and King.[111] The effect of hydrogen pressure at constant contact time and temperature is shown in Table XVII for 480° C, and

110 International Hydrogenation Patents Co., Ltd., Brit. Pat. 442,385 (1936).

111 Cawley, C. M., and King, J. G., *Dept. Sci. Ind. Research (Brit.), Fuel Research Board, Tech. Paper* 45 (1937), 45 pp.

TABLE XVII

Effect of Pressure on Hydrogenation of Low-Temperature Tar at 480° C [62]

Pressure, atmospheres	100	150	200	300	400
Gasoline yield percent by weight of tar	35.4	36.3	41.0	41.8	42.2

the effect of temperature at constant contact time and pressure is illustrated by the data of Table XVIII for both 200 and 400 atmospheres pressure. These data show that the gasoline yield increased with increasing hydrogen pressure for temperatures above about 430° C. Below this temperature, increased pressure had no observable effect on the specific gravity of the product or on the yield of gasoline. The maximum effect of increased pressure at 480° C appears to have been reached at about 350 atmospheres. At 480° C, an increase of about 25 percent in the amount of hydrogen consumed was noted in increasing the pressure from 200 to 400 atmospheres. Since the yield of gasoline increased only from 41.0 percent at 200 atmospheres to 42.2 percent at 400 atmospheres, it is apparent that the greater amount of hydrogen used was largely consumed in adding hydrogen to unsaturated and aromatic compounds. The effect of

increased pressure on the length of the period of satisfactory catalyst activity was quite large. The catalyst deterioration was 2.5 times slower at 400 atmospheres than at 200 atmospheres, despite the fact that the materials throughput was twice as great at the higher pressure.

Table XVIII contains some data on the effect of temperature on tar hydrogenation. Since the original tar contained 7.0 percent of gasoline, it is apparent that little if any reduction in molecular weight was obtained at 300° C. The cracking reaction became appreciable at 350° C, the gasoline yield increased steadily with temperature, and presumably the yield of normally gaseous hydrocarbons also increased with temperature, but the hydrocarbon yield was given for only one temperature and pressure, namely, about 14 percent for 480° C and 200 atmospheres. Comparison of the results at 200 and 400 atmospheres and 510° C in Table XVIII shows that increased pressure markedly increased the gasoline yield. The tar acids (or phenols) were not appreciably attacked at temperatures below 350° C; above this temperature they were readily hydrogenated to produce water and hydrocarbons.

Table XIX shows the effect of hydrogen to tar ratio at 480° C and 200 atmospheres.

TABLE XVIII

Effect of Temperature on Hydrogenation of Low-Temperature Tar at 200 and 400 Atmospheres [62]

(Percentages by weight of tar treated)

Pressure, atmospheres		Temperature, °C						
		300	350	390	430	450	480	510
200	Specific gravity	....	0.970	0.930	0.902	0.887	0.867	0.847
	Gasoline, percent	7.2	13.4	19.7	30.4	34.2	41.0	46.0
	Tar acids, percent	18.8	19.0	7.5	1.1	......	......	......
400	Specific gravity	....	0.970	0.930	0.893	0.875	0.847	0.815
	Gasoline, percent	....	... ..	20.7	30.6	35.5	42.2	56.0
	Tar acids, percent	....	......	8.5	1.2	......	......	.... .

TABLE XIX

Effect of Hydrogen-to-Tar Ratio on Hydrogenation of Low-Temperature Tar at 480° C and 200 Atmospheres Pressure [62]

Hydrogen-to-tar molecular ratio	13	16	19	22	37	52	97	158
Liquid product, specific gravity at 15° C	0.867	0.859	0.858	0.854	0.847	0.848	0.847	0.849
Yield of gasoline, per-cent by weight of dry tar	40.5	42.9	44.0	44.2	44.5	45.8	45.2	44.9

The specific gravity of the liquid product decreased rapidly with increasing hydrogen-to-tar ratio until that ratio reached about 40 (calculated on the basis of an average molecular weight of 250 for the tar). The gasoline yield increased to a maximum at a hydrogen-to-tar ratio of about 50.

The data of Table XX show that the yield of gasoline per pass decreased only

TABLE XX

Effect of Contact Time in Hydrogenation of Low-Temperature Tar at 480° C and 400 Atmospheres Pressure [62]

Time of contact, minutes	20	10	5	2 5	1.25
Liquid product, specific gravity at 15° C	0.811	0.832	0 847	0 859	0 882
Yield of gasoline, per-cent by weight of dry tar	56.3	47 5	42.5	41 3	36 5

slowly with decreasing contact time (volume of free space in the converter divided by the volume of gas and vapors passing per minute). Thus, by accepting a yield of 36.5 rather than 56.3 percent of gasoline at 400 atmospheres and 480° C, the volume of the converter may be reduced by a factor of about 10, that is, $\frac{20 \times 36.5}{1.25 \times 56.3}$. A further advantage of the shorter contact time is that the catalyst deterioration per volume of tar treated by 1 volume of catalyst decreases with decreasing contact time.

Results obtained in the British Fuel Research Laboratory [111] with various tars are presented in Table XXI. The gasoline yield decreased rapidly with increasing pitch content of the tar, and the rate of catalyst deterioration increased. For high-temperature tars the rate of catalyst deterioration was fast enough to make it profitable to employ two stages of hydrogenation, that is, to start with liquid-phase operation in which a small amount of powdered catalyst is continuously pumped into the converter along with the tar at a reaction temperature of about 450° C.

Very little information has been published on the hydrogenation of high-temperature tars. King [62] stated that horizontal-oven tar is more difficult to hydrogenate than the product from vertical ovens. He also presented some results obtained by Chemical Reactions, Ltd., in Great Britain on the liquid-phase hydrogenation of high-temperature tars. These results were obtained by using 0.5 percent of a catalyst (composition not disclosed) finely dispersed in the tar, 200 atmospheres pressure of hydrogen, and 430 to 440° C. The converter capacity was 5 liters, and the throughput 600 cubic centimeters per hour. The greater proportion of the products vaporized and was carried out of the converter in the stream of hydrogen; the remainder was withdrawn as a liquid. The results are summarized in Table XXII.

TABLE XXI

Yields and Catalyst Deterioration for Different Tars [111]

(480° C and 200 atmospheres; percentages by weight of dry, raw material)

Origin of Tar	Specific Gravity of Tar at 15° C	Percentage of Pitch (Material Boiling above 360° C)	Percentage of Tar Acids in Raw Material *	Percentage of Neutral Oil to 200° C in Tar	Specific Gravity of Hydrogenated Tar at 15° C	Yield of Gasoline or Neutral Oil to 200° C	Catalyst Deterioration †
Dalton main coal, Parker retort	1.035	39.3	22.3	4.6	0.868	38.0	0.8
Dalton main coal, Fuel Research Laboratory cast-iron retorts	1.049	45.8	18.3	7.1	.896	32.9	0.5
Dalton main coal, Fuel Research Laboratory brick retorts, 5.7 tons per retort per day	1.058	41.5	19.3	7.3	.890	41.2	1.2
Dalton main coal, Fuel Research Laboratory brick retorts, 10 tons per retort per day	1.073	47.4	15.4	5.4	.905	30.1	1.3
Glover-West retorts, 18 percent of steam used during carbonization	1.054	50.5	14.6	3.4	.898	27.5	2.1
Glover-West retorts	1.077	51.2	10.6	2.0	.920	22.9	3.8

* The tar-acid content of the hydrogenated tar was about 0.5 percent in all cases.

† Decrease in gasoline yield in percentage per 10 volumes of raw material per volume of catalyst.

The most sensitive index of the change produced by hydrogenation is the "naphtha-insoluble, benzene-soluble" data. It is apparent that these figures are reduced considerably by hydrogenation. The hydrogenation product contains no pitch in the usual sense of the word, for the fraction boiling above 360° C is a distillable oil.

Cawley [112] presented some data on the liquid-phase hydrogenation of both low- and high-temperature tars, using 0.5 percent molybdic acid and 0.5 percent stannous chloride as catalysts, 200 atmospheres pressure of hydrogen, and 450° C. His results show that stannous chloride is a much better catalyst than molybdenum trioxide for the hydrogenation of high-temperature tar. The British Fuel Research Board has reported the results of experiments at 450° C and 200 atmospheres pressure on

112 Cawley, C. M., *Gas World*, **103**, Coking Sect., 31–6 (1936).

TABLE XXII

Liquid-Phase Hydrogenation of High-Temperature Tars [62]

	Topped Coke-Oven Tar		Topped Vertical-Retort Tar		Topped Horizontal-Retort Tar		Topped Chamber-Oven Tar	
	Original	Hydrogenated	Original	Hydrogenated	Original	Hydrogenated	Original	Hydrogenated
Specific gravity of tar	1.167	1.085	1.075	1.015	1.195	1.122	1.143	1.054
Yield percent by volume	....	98	....	96	....	94	....	98
Naphtha *-insoluble, benzene-soluble	57.0	19.5	35.0	8.1	42.5	29.0	53.0	8.8
Naphtha-insoluble, benzene-insoluble	8.0	2.5	8.8	1.7	13.5	9.4	17.5	0.9
Oil to 360° C	38	54	69	78	25	54	48	73
Pitch	60	41	28	19	73	44	50	26
Specific gravity oil to 360° C	....	1.005	....	0.981	....	1.030	....	1.028
Tar acids in oil to 360° C	....	10.2	....	17.5	....	11.0	....	16.9

* Petroleum solvent naphtha, b.p. 100 to 110° C.

the liquid-phase hydrogenation of high-temperature vertical-retort tar in an experimental plant.[113] The throughput was 200 cubic centimeters per hour of tar (600-cubic centimeters converter capacity) made by the carbonization of a Yorkshire gas coal. This tar hydrogenated almost as readily as low-temperature tar. Tests using 0.1 to 0.5 percent of various catalysts (molybdenum trioxide, hydrochloric acid, stannous chloride, and hydriodic acid) showed that the most satisfactory one was a mixture of 0.1 percent molybdenum trioxide plus an equal quantity of hydriodic acid. Experiments with recycling of high-boiling products for both low- and high-temperature tars from vertical retorts yielded the results shown in Table XXIII.[114]

TABLE XXIII

RESULTS OF LIQUID-PHASE TAR
HYDROGENATION [114]

	Low-Temperature Vertical-Retort Tar	High-Temperature Vertical-Retort Tar
Yield of oils (percent by weight of dry tar):		
Gasoline to 170° C	15.0	12.2
Middle oil 170 to 300° C	68.2	70.1
Oil boiling above 300° C	3.9	3.8

The British Fuel Research Laboratory reported also the results[114] of some preliminary experiments on the liquid-phase hydrogenation of coke-oven tar made by the carbonization of Parkgate Seam slack coal. The temperature in the hottest point in the oven was about 1,250° C. The tar was of 1.17 specific gravity at 15° C, the free carbon and asphalt contents were 5.1 and 45.9 percent respectively, and the residue boiling above 360° C ("pitch") was 60 percent. This tar was hydrogenated in a continuously operating experimental plant with a capacity of 1 to 4 liters of tar per hour, and in the presence of 0.1 percent each of hydrogen iodide and molybdic acid as catalysts. The product was described as a dark greenish brown oil (specific gravity at 15° C, 0.985) containing 0.2 percent of free carbon and 1.8 percent of asphalt. The yield was 92.4 percent by weight of the tar. The residue boiling above 360° C was a thick dark brown oil and amounted to 15.6 percent by weight of the tar.

Some experiments have been made in the Bureau of Mines experimental plant at Pittsburgh, Pa., with topped (to 235° C) high-temperature tar from byproduct coke ovens.[115] A catalyst found well suited for the liquid-phase operation was 0.05 percent of iodoform. The throughput in the liquid phase was approximately 2 liters per hour, the converter capacity about 7.5 liters, the temperature 445° C, pressure 4,000 pounds per square inch, and hydrogen input about 400 cubic feet per hour. Five continuous liquid-phase runs of about 100 hours each indicated that it was possible to hydrogenate the topped tar with a combined recycle (centrifuged heavy oil plus bottoms [over 300° C] from the distillation of product vaporized in a stream of hydrogen) of about 50 percent of the total feed.

The analysis and yield of the fraction of the product boiling up to 207° C are shown in Table XXIV. About 95 percent of the total product boiled below 330° C and contained 3 percent of tar acids, 1.5 percent tar bases, and the neutral oil contained 75 percent aromatic hydrocarbons, 23 percent saturated hydrocarbons (paraf-

113 Dept. Sci. Ind. Research (Brit.), Fuel Research Board, Rept. for Year Ended March, 1938, pp. 150–8.

114 Dept. Sci. Ind. Research (Brit.), Fuel Research Board, Rept. for Year Ended March, 1939, pp. 134–7.

115 Storch, H. H., Hirst, L. L., Fisher, C. H., Work, H. K., and Wagner, F. W., Ind. Eng. Chem., 33, 264–74 (1941).

TABLE XXIV

PRODUCTS FROM HYDROGENATION OF TOPPED HIGH-TEMPERATURE TAR [115]

Substance	Products from Liquid-Phase Hydrogenation		Products from Vapor-Phase Hydrogenations			
	Concentrations in Overhead * Oil	Yield Based on Topped Tar	Concentrations in Overhead * Oil		Yield ‡ Based on Topped Tar	Total Recycle Yield Based on Topped Tar
			Actual	Corrected †		
	vol. %	vol. %	vol. %	vol. %	vol. %	vol. %
Phenol	0.26	0.27	0.0	0.0	0.0	0.27
Cresol	0.74	0 76	0.0	0.0	0.0	0.76
Benzene	0.50	0.51	0.64	0.38	1.19	1.70
Toluene	1.64	1.69	2.17	1.27	3.98	5.67
Xylene	1.83	1.87	2.19	1.28	4.00	5.87
Tetrahydronaphthalene	1.36	1.40	5.23	3.07	9.60	11.00
Cyclohexane	0.57	0.59	0.85	0.50	1.56	2.17
Methylcyclohexane	1.14	1.18	1 28	0.75	2.35	3.51
Dimethylcyclohexane	0.57	0.59	0.50	0.29	0.91	1.50
High-flash naphtha	18.09	18.64	25.84	15.16	47.41	66.05
Total oil distilling to 207°)	26.70	27.50	38.70 †	22.70	71 00	98.50

* Overhead oil is the oil distilling in the stream of hydrogen passing through the liquid-phase converter. It is the steady-state raw product from which the final products are separated by distillation.

† The feed stock to the vapor-phase converter contained about 16 percent distilling to 270° C. If this had been completely removed, the concentrations of the various chemicals in the vapor-phase overhead oil would have been about as listed in the "corrected" column.

‡ Calculated by assuming a steady-state concentration of 22.7 percent of overhead oil distilling to 207° C. The overall volume yield in the vapor phase of oil distilling below this temperature is $(103 - 27.50) \times 0.94 = 71.0$ percent, where 27.50 is the percent yield of oil distilling to 207° C in the liquid-phase product, 103 is total liquid-phase-oil yield in volume percent of the topped tar, and 0.94 is the vapor-phase yield of oil distilling to 207° C as volume percent/100 of the liquid-phase product boiling above 207° C.

fins plus naphthenes), and 2 percent olefins. In the vapor phase the feed stock was the 207 to 300° C fraction from the liquid-phase operation. The catalyst was alumina gel impregnated with ammonium molybdate to about 25 percent of its weight, and this was dried and heated in air at 500° C before use. The throughput was about 4 pounds (1.9 liters at 20° C) per hour, and the catalyst volume 170 cubic centimeters. During two runs of about 60 hours each, vapor contact times of 0.3 to 0.5 minute, temperatures of 490 to 515° C, and hydrogen-to-vapor ratios of 15 to 37 were investigated. No unusual difficulties were experienced. The fraction of the product boiling above 207° C was recycled. The analysis of the product and the yield are shown in Table XXIV. The high-flash naphtha listed in this table consisted largely of polymethylbenzenes and polymethylcyclohexanes.

Data on the feed stock and products of the vapor-phase hydrogenation of middle oils from hydrogenated low- and high-temperature, vertical-retort tars are presented [114] in Tables XXV, XXVI, and XXVII. The experiments were carried out in a continuously operating experimental plant with a capacity of 1 to 4 liters per hour of tar, with pelleted molybdenum disulfide as catalyst. For the production of gasoline, the optimum conditions were 415° C, 200 atmospheres pressure, and a throughput of 1 volume of oil per volume of catalyst per hour, using as feed stock 200 to 300° C middle oil from liquid-phase hydrogenation (see Table XXV).

The properties and yields of liquid- and vapor-phase gasolines are shown in Table

TABLE XXV

PROPERTIES OF MIDDLE OILS FROM LIQUID-PHASE TAR HYDROGENATION [114]

	Low-Temperature Vertical-Retort Tar	High-Temperature Vertical-Retort Tar
Specific gravity at 15° C	0.931	0.931
Analysis of oil (percent by weight):		
Tar acids	19.3	13.2
Tar bases	2.2	1.7
Neutral oil	78.5	85.1
Carbon	86.7	87.5
Hydrogen	10.2	10.3
Nitrogen	0.2	0.2
Sulfur	0.2	0.1
Oxygen	2 7	1.9
Distillation of neutral oil (percent by weight of middle oil)		
To 170° C	5.4	3.3
170–200°	11.2	7.3
200 230°	19.7	21.9
230–270°	27.0	33.7
270 300°	11.9	14.4
Residue	2.8	4.1

TABLE XXVI

YIELD AND PROPERTIES OF GASOLINES FROM TAR HYDROGENATION [114]

	Low-Temperature Tar		High-Temperature Tar	
	Vapor-Phase	Liquid-Phase	Vapor-Phase	Liquid-Phase
Specific gravity at 15° C	0.742	0.795	0.734	0.783
Distillations (volume percent)				
Initial boiling point, °C	46	50	41	52
to 50°	0.5	0	1	0
75°	10	1	15	1
100°	39	13.5	44	22
125°	72	52	75	59.5
150°	91	81	90	82.5
175°	98	92	....	92
Final boiling point, °C	188	202	174	207
Total distillate	98.5	97	98	97
Residue	0.5	2	1	2
Loss	1	1	1	1
Analyses (weight percent)				
Aromatics	0	34	0	24
Unsaturates	0	2	0	3
Saturates	100	64	100	73
Carbon	85.0	86.9	84.9	86.5
Hydrogen	14.8	12.5	15.0	13.0
Sulfur	0.0	0.1	trace	0.1
H/C atomic ratio	2.09	1.73	2.12	1.80
Octane number (C.F.R. motor method)	66	71	66	70
Gasoline to 170° C (weight percent of tar)	56.1	15.0	61.1	12.2
Total yield of gasoline to 170° C				
Weight percent of tar	71.1		73.3	
Volume percent of tar	94.5		98.8	

XXVI. The vapor-phase products were good gasolines of 66 octane number, but the liquid-phase gasolines were deficient in volatile constituents and could be used only for blending. The liquid-phase middle oils were rather low-boiling for use as Diesel fuel, and a light fraction had to be removed to raise the flash point sufficiently. Another and more serious defect in this oil for use as Diesel fuel was the poor ignition quality due to the low hydrogen-to-carbon ratio. The object of the second stage of hydrogenation for Diesel oil production was to effect the addition of hydrogen with the least possible reduction in boiling range of the oil. Sufficient hydrogen, however, could be added only at a temperature at which substantial degradation of molecular size occurs. Thus, suitable conditions for the production of Diesel oils from the middle oils were found to be: 380° C, 200 atmospheres pressure, and a throughput of 2 volumes of oil per volume of catalyst per hour. Under these conditions the middle oils yielded about 50 percent of a Diesel oil fraction. The properties of these Diesel fuels are given in Table XXVII. Since the cetene number of these oils was only 45, these oils are of poor quality for Diesel service.

DESIGN AND MATERIALS FOR CONSTRUCTION OF COAL- AND TAR-HYDROGENATION EQUIPMENT

Although several experimental plants have been described in some detail,[13, 15, 16, 17, 106, 109] only very general descriptions of industrial-size plants [18, 19, 20] are available. Some of the development work at

TABLE XXVII

Yield and Properties of Diesel Oils from Tar Hydrogenation [114]

	Diesel Oil from Low-Temperature Tar	Diesel Oil from High-Temperature Tar
Specific gravity at 15° C	0.862	0.868
Distillations (weight percent)		
Initial boiling point °C	194	194
to 200°	0	0
225°	48	37.5
250°	80	74
275°	93.5	92
300°	. . .	97
Final boiling point °C	294	302
Total distillate	97.5	97.5
Residue	2	2
Loss	0.5	0.5
Analyses (weight percent)		
Carbon	86.8	87.0
Hydrogen	12.9	12.9
Sulfur	0.3	0.1
H/C atomic ratio	1.78	1.78
Aniline point °C	46.1	44.6
Flash point °F	155	156
Cetene number	45	45
Yield (percent by weight of middle oil)	45.7	55.3
Yield (percent by weight of original tar)	32.7	40.5

the I. G. Farbenindustrie A.-G., with pilot plants, has been discussed by Pier.[116] For the liquid-phase hydrogenation of heavy oils, tars, and coal with finely divided catalysts, some experiments were carried out in autoclaves, but most of the work was done with special converters arranged for continuous operation. These converters had capacities of several liters. The pilot plant was of such size that its throughput was 300 times that of the small-scale plants (or 300 times "several" liters), and about one-tenth to one-twentieth of that for the proposed full-scale plants. Several pilot-plant converters 300, 500, and 800 millimeters (12, 20, 32 inches) in diameter with reaction volumes up to 3 cubic meters (106

cubic feet) were used. The full-sized industrial units have reaction volumes of 30 to 60 cubic meters (1,060 to 2,120 cubic feet).

Some details of the construction of the Billingham plant have been given by Smith.[117] This plant contains five units or "stalls" (see Figs. 4 and 5), each containing three converters, heat exchanger, traps, piping, and control equipment. The converter is a nickel-chromium-molybdenum steel cylinder 4 feet 9 inches in inside diameter; the length, including the two closures, is 43 feet 2 inches. The closures are conical-shaped reducers attached to the converter by a Vickers-Anderson-type [118] joint. A hollow-steel ring is employed as the sealing member in such a way that once a gas-tight joint has been made the gas pressure inside the converter expands the ring and seals the joint. Converters are forgings carefully heat-treated.

For maintenance, a 170-ton crane with a 48-foot radius and hook level 97 feet above track carries the converters or other large pieces of equipment to the maintenance house. The maintenance house has 82 feet of head room and is provided with a pit 45 feet deep, into which the converters can be lowered, and an overhead 170-ton crane identical with the one for transporting the converter to the maintenance house is used to withdraw the complete internal fittings of the converter.

In large-scale coal-hydrogenation converters the destructive action of high-pressure hydrogen at elevated temperatures on ordinary steel is avoided by a system involving thermal insulation of the heavily stressed steel parts. For preheaters where the double-wall principle cannot be applied,

116 Pier, M., *Chem. Fabrik*, 8, 45–54 (1935); *Fuel*, 14, 136–44 (1935).

117 Smith, F. E., *Engineering*, 141, 648–9, 680–2 (1936).

118 Tongue, H., *Design and Construction of High-Pressure Chemical Plant*, Chapman and Hall, London, 1934, pp. 204–5.

metallurgical research has resulted in the development of alloy steels resistant to hydrogen embrittlement.[119] Below 400° C, when the hydrogen pressure does not exceed 50 atmospheres, good grades of carbon steels with normal sulfur and phosphorus contents can be used. Steels containing 2.5 percent chromium and 0.5 percent molybdenum can be used over the temperature range 350 to 400° C under 300 to 400 atmospheres hydrogen pressure. At higher temperatures a slow decarburization occurs, which can be observed even under 100 atmospheres at 450° C. Although 6 percent chromium steels are fairly resistant to corrosion by hydrogen at 400 to 600° C and 300 atmospheres pressure, it is only when the chromium content reaches about 12 percent that the corrosion becomes negligible. The addition of molybdenum to low-chrome steels increases their resistance to corrosion and their mechanical stability at elevated temperatures. Steel containing 5 percent chromium and 0.5 molybdenum resists the action of hydrogen up to 600° and 250 atmospheres, and prolonged heating at 350° neither increases the grain size nor renders it fragile. The addition of vanadium to the extent of about six times the carbon content of a steel causes a very sharp increase in its resistance to hydrogen corrosion. The elements chromium, molybdenum, vanadium, tungsten, and titanium decrease the corrosive effects of hydrogen on metals by the formation of stable carbides or by retarding the diffusion and solution of hydrogen in the metal.

Chromium is most effective in raising the creep (permanent deformation due to stress) strength of steel.[120] A low-carbon steel containing about 5 percent chromium and 0.5 percent of molybdenum has more than twice the creep strength of ordinary carbon steel at 540° C. Combined with nickel in varying proportions, chromium produces the best commercial refractory ferrous alloys. These alloys are further improved by small additions of molybdenum, tungsten, titanium, etc. The well-known alloy "18–8," which contains from 18 to 20 percent chromium and 8 to 10 percent nickel, has excellent creep strength. It belongs to the class of austenitic alloys having a face-centered cubic lattice, whereas ordinary steels are body-centered. Although the austenitic steels are comparatively soft at atmospheric temperature, they are far stronger at higher temperatures than the ferrito-pearlitic type of steel. The loss of ductility associated with austenitic high-chromium-nickel-type steel when stressed at temperatures between 500 and 850° C appears to be due to the precipitation of carbide in the form of a membrane surrounding the austenitic grains, thereby producing intergranular weakness. This loss of ductility can usually be avoided by the addition of the stabilizing elements columbium or titanium, which prevent the carbide precipitation.

The use of corrosion-resistant linings in coal-hydrogenation converters has been covered by a number of patents, for example, alloys containing 70 to 85 percent of silver,[121] coating the interior of the re-

119 Cox, J., *Trans. Am. Inst. Chem. Engrs.*, **29**, 43–85 (1933). Barber, A. T., and Taylor, A. H., *Engineering*, **138**, 576–8, 635–6 (1934). Wolfsohn, S. I., and Miagkov, M. P., *Vestnik Matalloprom.*, **16**, 67–72, 82–8 (1936); *Chimie & industrie*, **37**, 487 (1937). Winter, H., *Glückauf*, **73**, 420–4 (1937). Naumann, F. K., *Tech. Mitt. Krupp, Tech. Ber.*, **1938**, 71–87; *Chem. Fabrik*, **1938**, 365–76; *Stahl u. Eisen*, **58**, 1239–50 (1938).

120 *Creep Data. Compilation of Available High-Temperature Creep Characteristics of Metals and Alloys*, Am. Soc. Mech. Engrs., New York, and Am. Soc. Testing Materials, Philadelphia, 1938, 860 pp.

121 International Hydrogenation Patents Co., Ltd., Brit. Pat. 453,419 (1936).
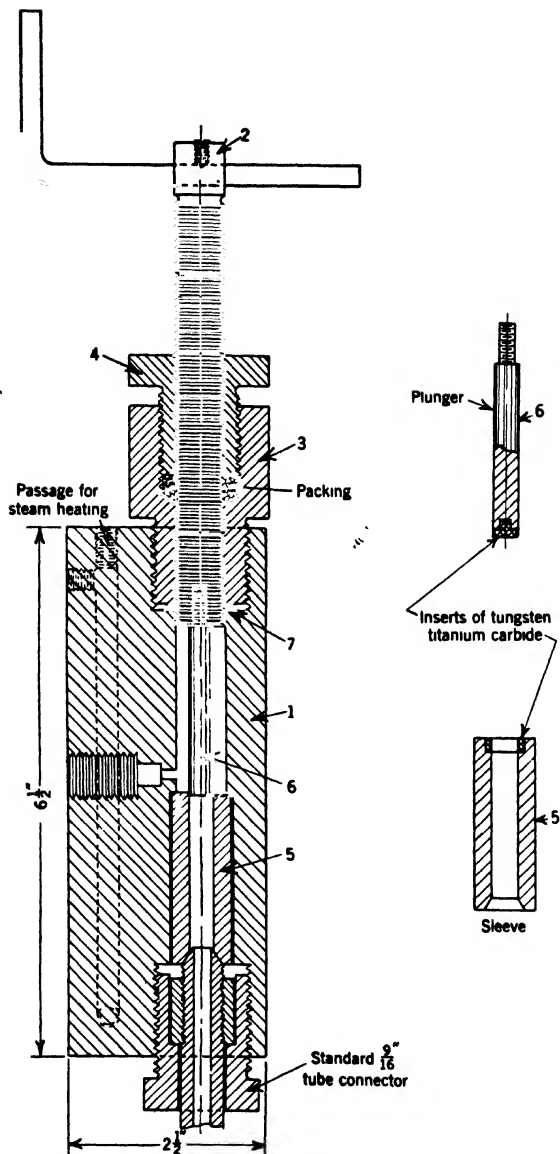
FIG. 8.   Throttling valve with interchangeable inserts in sleeve and plunger for discharging heavy oil slurry.

action vessel with zinc [122] or cadmium [123] or their alloys, high-chromium-nickel steels [124] and tantalum and its alloys.[125]

Perhaps the most difficult of the engineering tasks involved in coal hydrogenation are coal-oil paste pumping and discharge of heavy-oil slurry containing the coal ash, unreacted coal, and catalyst particles. At Billingham [117] the high-pressure paste pumps are operated by a hydraulic system working at 600 pounds per square inch. Experimental plants in Great Brit-

[122] I. G. Farbenindustrie A. C., Ger Pats. 637,-237 (1936), 626,461 (1937).

[123] International Hydrogenation Patents Co., Ltd., Fr. Pat. 800,957 (1936) ; Brit. Pat. 458,667 (1936).

[124] I. G. Farbenindustrie A.-G., Ger. Pat. 655,-324 (1938). Cockram, C., Holroyd, R., and Imperial Chemical Industries, Ltd., Brit. Pat. 433,-020 (1935). Standard I. G. Co., U S Pat. 1,-949,631 (1934).

[125] International Hydrogenation Patents Co., Ltd , Brit. Pat. 427,435 (1935).

tain [13'] and the United States [17] have reported difficulty with paste pumping on account of the "gelling" and "drying" of the paste. When first prepared, the paste was oily to the touch and flowed freely under gravity. Where drying occurred, the paste was dull and crumbled readily when touched. Such drying makes paste pumping mechanically impossible. It can be avoided by using a specially selected heavy-oil fraction for pasting purposes and by avoiding finely powdered coal; minus 80 mesh with a minimum of minus 200 mesh coal appears to be most desirable. Even when drying was not experienced, the paste was sometimes found to flow with difficulty under gravity alone from the paste tank to the pump, in spite of wide-bore piping The paste set like a gel in the pipe; this action could be avoided by continuous circulation of the paste by a

FIG. 9. All-purpose throttling valve.[17]

low-pressure pump so as to provide a posi-
tive pressure at the intake of the high-
pressure pump and also to keep the paste
agitated. The high-pressure paste-pump
units usually consist of a cylinder and loose-
fitting plunger with ball check valves[126] at
the inlet and outlet sides.

Discharge of liquids that contain solid
materials in suspension and gases in solu-
tion from high-pressure vessels involves se-
vere erosion of metal parts. Special valves
have been designed for this service,[17, 127]
and the use of the very hard carbides of
tungsten and titanium for construction of
the metal parts in contact with the slurry
has solved this difficult problem. The
valve shown in Fig. 8 was designed at the
Bureau of Mines experimental coal-hydro-
genation plant for heavy-oil-slurry dis-
charge. It has given very satisfactory
service, particularly since the plunger and
sleeve (parts 6 and 5) were fitted with in-
serts of tungsten-titanium carbide. The
success of this valve depends on obtaining
an excellent fit of the plunger in the sleeve.
A poorly fitted valve will have only one-
tenth the life of a well-fitted one. Once

126 I. G. Farbenindustrie A.-G., Brit. Pat. 459,-
662 (1937).

127 Uhde, F., Brit. Pat. 457,447 (1936).

the plunger is wet with the slurry, a half
to a quarter turn of the plunger, which
amounts to withdrawal of about 0.02 inch,
permits slurry to flow from the converter
at about the optimum rate. When the
discharge is complete, a quarter to a half
turn in the opposite direction closes the
valve to the passage of gas. When fitted
with hardened tool-steel plunger and sleeve,
the life period was about 300 hours;
whereas, when inserts of tungsten-titanium
carbide were made, as shown in Fig. 8, the
life period was about 3,000 hours.

Figure 9 shows an all-purpose valve with
replaceable needle and seat developed at
the Bureau of Mines experimental coal-hy-
drogenation plant.[17] The valve as shown
is arranged for service as a shut-off valve
in the heavy-oil-slurry line. It can, how-
ever, also be fitted with a gas-throttling
type of needle and seat when precise con-
trol of gas flow is required; or a floating
ball may be used on the stem with the
regular seat when a comparatively fast
opening or closing valve is needed. It is
necessary to tighten the seat against its
sealing gasket, part 8, if the seat loosens in
service. The stem packing is a preformed
ring, which can be easily replaced.

SYNTHESIS OF HYDROCARBONS FROM WATER GAS *

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The possibility of producing aliphatic hydrocarbons other than methane by the catalytic reduction of carbon monoxide was disclosed by the Badische Anilin und Soda Fabrik in 1913 and by Fischer and Tropsch in 1923.[1] For several years Fischer and Tropsch had been studying the reduction of carbon monoxide in the presence of alkali-iron catalysts at 400 to 450° C and 100 to 150 atmospheres pressure.[1] "Synthol," which was the product of this reaction, consisted of a mixture of alcohols, aldehydes, fatty acids, and hydrocarbons. Fischer and his coworkers observed that the content of oxygenated compounds of synthol decreased with decreasing pressure, and that the liquid product obtained at pressures below about 7 atmospheres was mainly a mixture of olefinic and paraffinic hydrocarbons. However, since the reaction velocity decreased rapidly with decreasing pressure, it was essential to hunt for more active catalysts.

In 1925–6 Fischer and Tropsch[2] and

Fischer[3] published results obtained by the use of more active catalysts prepared from iron or cobalt mixed with various supporting materials, and of mixtures of hydrogen and carbon monoxide at atmospheric pressure and at temperatures from 250 to 300° C. The organic product was almost free from oxygenated compounds and consisted largely of hydrocarbons ranging from ethane to solid paraffins. Fischer thought that a likely mechanism of this chemical reaction was the initial formation of metallic carbides and either water or carbon dioxide and subsequent production of paraffins by reaction between the carbides and hydrogen to produce methylene, which was at once polymerized to higher hydrocarbons. Despite the fact that paraffinic hydrocarbons above ethane could not be produced by passing hydrogen alone over the metal carbides, later work has provided considerable support for the reaction mechanism postulated by Fischer.

Elvins and Nash[4] also reported the formation of oily material on a cobalt-copper-manganese oxide catalyst at atmospheric pressure and at temperatures from 245 to 284° C. The yields were small, and the

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[1] Badische Anilin u. Soda Fabrik, Ger. Pat. 293,787 (1913). Fischer, F., and Tropsch, H., *Brennstoff-Chem.*, **4**, 276–85 (1923).

[2] Fischer, F., and Tropsch, H., Ger. Pat. 484,-337 (1925); *Brennstoff-Chem.*, **7**, 97–104 (1926); *Ber.*, **59**, 830–1, 832–6, 923–5 (1926).

[3] Fischer, F., *Proc. 1st Intern. Conf. Bituminous Coal*, 234–46, 1926.

[4] Elvins, O. C., and Nash, A. W., *Fuel*, **5**, 263–5 (1926); *Nature*, **118**, 154 (1926). Nash, A. W., *J. Soc. Chem. Ind.*, **45**, 876–81 (1926).

product included some oxygen-containing compounds in addition to hydrocarbons. Subsequent work by Fischer and Tropsch [5] confirmed the presence of oxygenated organic compounds in the product from the atmospheric-pressure synthesis and showed [6] that at 10 to 15 atmospheres pressure the products were intermediate in nature; at atmospheric pressure the product consisted largely of hydrocarbons, and at high pressures, mainly of oxygenated compounds.

Smith, Davis, and Reynolds [7] reported the presence of olefinic as well as paraffinic hydrocarbons in the product. At about the same time, Elvins [8] and Erdely and Nash [9] published the results of further work on the preparation and activity of various catalysts and on the nature of the products obtained at atmospheric pressure and at 280 to 320° C.

In 1928, Fischer and Tropsch [10] reported the results of an extensive examination of the gaseous and liquid hydrocarbon products of the synthesis at 190° C on an iron-copper catalyst at atmospheric pressure. No hydrocarbons other than olefins and paraffins were found. The gaseous product contained ethane, 42.5; propane, 19.5; butane, 2.0; ethylene, 6.0; propylene, 21.0; and butylene, 9.0 volume percent. The liquid product boiling between 60 and 185° C contained 30 percent paraffins, for the most part octane, nonane, and isononane, which were positively identified. The

remaining 70 percent were olefins. No diolefins were present. No analytical work other than examination for unsaturates was done on the higher-boiling liquid product. Water-soluble oxygenated products amounted to 2 percent of the total products. In the same year (1928), Smith, Hawk, and Reynolds [11] presented detailed data on the yield of olefinic and paraffinic hydrocarbons on a cobalt-copper-manganese oxide catalyst at temperatures of 200 to 260° C. The lower hydrocarbons were analyzed completely. Further examination of the hydrocarbon product by Tropsch [12] and Tropsch and Koch [12] resulted in the identification of various olefinic and paraffinic hydrocarbons; it showed the absence of naphthenes but the presence of small quantities of benzene and toluene.

Some additional work on high-pressure synthesis was done by Audibert and Raineau [13] with catalysts such as iron phosphate or iron borate at about 150 atmospheres. The products were mixtures of hydrocarbons and oxygenated organic compounds, chiefly alcohols. Catalysts for the atmospheric-pressure synthesis were developed by Kodama,[14] who found that the activity of nickel and of cobalt catalysts was enhanced by the promoters copper, thorium dioxide, and magnesia.

In hunting for clues as to the reaction mechanism of the synthesis of hydrocarbons by the reduction of carbon monoxide, Smith, Hawk, and Golden [15] found that

5 Fischer, F., and Tropsch, H., Ger. Pat. 524,-468 (1926); *Brennstoff-Chem.*, **7**, 299–300 (1926), **8**, 1–5 (1927); *Ber.*, **60**, 1330–4 (1927).

6 Fischer, F., and Tropsch, H., *Brennstoff-Chem.*, **8**, 165–7 (1927).

7 Smith, D. F., Davis, J. D., and Reynolds, D. A., *Ind. Eng. Chem.*, **20**, 462–4 (1928).

8 Elvins, O. C., *J. Soc. Chem. Ind.*, **46**, 473-8T (1927).

9 Erdely, A., and Nash, A. W., *ibid.*, **47**, 219-23T (1928).

10 Fischer, F., and Tropsch, H., *Brennstoff-Chem.*, **9**, 21–24 (1928).

11 Smith, D. F., Hawk, C. O., and Reynolds, D. A., *Ind. Eng. Chem.*, **20**, 1341–8 (1928).

12 Tropsch, H., *Ges. Abhandl. Kenntnis Kohle*, **9**, 561–70 (1928-9). Tropsch, H., and Koch, H., *Brennstoff-Chem.*, **10**, 337–46 (1929).

13 Audibert, E., and Raineau, A., *Ann. combustibles liquides*, **3**, 367–428 (1928); *Ind. Eng. Chem.*, **21**, 880–5 (1929).

14 Kodama, S., *J. Soc. Chem. Ind., Japan*, **32**, Suppl. Binding, 4, 6, 23, 285 (1929), **33**, Suppl. Binding, 60, 202, 399 (1930).

15 Smith, D. F., Hawk, C. O., and Golden, P. L., *J. Am. Chem. Soc.*, **52**, 3221–32 (1930).

ethylene reacts in admixture with carbon monoxide and hydrogen on a cobalt-copper-manganese oxide catalyst to form large quantities of higher hydrocarbons and of oxygen-containing compounds which dehydrate in the process to form hydrocarbons. The dehydration may be accompanied by polymerization. Alone, or in admixture with either carbon monoxide or hydrogen, ethylene does not form higher hydrocarbons when passed over the cobalt-copper-manganese oxide catalyst at 200 to 250° C and atmospheric pressure. These experimenters also found that the mechanism of hydrocarbon formation on an iron-copper catalyst was essentially different from that on a cobalt-copper-manganese oxide catalyst, as ethylene did not enter into reaction on the iron-copper catalyst. They also found that the iron-copper catalyst produced largely carbon dioxide along with the hydrocarbons instead of water, which was the main oxygenated product from the copper-cobalt-manganese oxide catalyst.

Experimental work on the properties of iron-copper catalysts was done by Kodama [16] and Fujimura.[16] Fujimura also studied the preparation and properties of copper-cobalt catalysts promoted with oxides of magnesium, thorium, tungsten, uranium, molybdenum, and chromium.[17] Fischer and his coworkers [18] also studied nickel and cobalt catalysts, using thoria and manganese oxide as promoters. By improved methods of preparation the activity of these catalysts was increased until

at about 200° C a yield of liquid hydrocarbons of 100 to 153 cubic centimeters per cubic meter of gas mixture or 71 percent of the theoretical was obtained. Fujimura and Tsuneoka [19] obtained 145 cubic centimeters per cubic meter using a cobalt-copper-thorium-uranium (1 : 8 : 0.2 : 0.1) catalyst.

In 1932, Fischer and his coworkers considered their process sufficiently well developed on a laboratory scale to merit pilot-plant experimentation. Various technically available gas mixtures for the synthesis were examined both practically and theoretically.[20] The most practical process at that time seemed to be the conversion of coke-oven gas with steam over coke. Organic sulfur was removed by heating the synthesis gas to 400° C in the presence of an iron catalyst and subsequently scrubbing with alkaline ferricyanide solution. The catalyst employed was nickel-manganese-aluminum oxide supported on kieselguhr by precipitating from the nitrates with potassium carbonate and subsequent washing, drying, and reduction. The operating temperature was specified as 190 to 210° C, and the pressure 1 atmosphere. The catalyst was revivified every 1,000 hours by extraction of the solid paraffin with gasoline. The catalyst chambers were narrow boxes 1.2 by 120 by 500 centimeters. They were suspended in an oil bath for purposes of temperature control.[21] The gasoline product of the synthesis contained 15 to 38 percent of unsaturated hydrocarbons, the remainder being mainly straight-chain hydrocarbons; its octane number was 58. Sulfur and gumming compounds were ab-

16 Kodama, S., *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **14**, 169–83 (1930). Kodama, S., and Fujimura, K., *J. Soc. Chem. Ind., Japan*, **34**, Suppl. Binding, 14–6 (1931). Fujimura, K., *ibid.*, **34**, Suppl. Binding, 136–8, 227–9 (1931).
17 Fujimura, K., *ibid.*, **34**, 384–6 (1931), **35**, 179–82 (1932).
18 Fischer, F., *Brennstoff-Chem.*, **11**, 489–500 (1930). Fischer, F., and Meyer, K., *ibid.*, **12**, 225–8 (1931). Fischer, F., and Koch, H., *ibid.*, **13**, 61–8 (1932).

19 Fujimura, K., and Tsuneoka, S., *J. Soc. Chem. Ind., Japan*, **35**, Suppl. Binding, 415–6 (1932).
20 Fischer, F., Pichler, H., and Reder, R., *Brennstoff-Chem.*, **13**, 421–8 (1932).
21 Fischer, F., Roelen, O., and Feisst, W., *ibid.*, **13**, 461–8 (1932).

sent. The fraction of the oil product boiling above 220° C was better than gas oil for Diesel fuel. The melting point of the solid paraffin was 48° C. These materials were produced [22] in the ratio of gasoline : oils boiling above 220° : paraffin = 4 : 1 : 0.2.

INDUSTRIAL DEVELOPMENT

The decade of research by Fischer and others outlined above so improved the catalyst activity and increased the technical development of the synthesis of hydrocarbons from carbon monoxide and hydrogen that, in 1933, the Ruhrchemie A.-G. undertook the construction of a plant of 1,000 tons per year capacity.[23] This plant was erected in Oberhausen-Holten, Ruhr, Germany. It was designed to produce motor fuel and lubricating oil.[24] The synthesis gas consisting of 1 part of carbon monoxide and 2 parts of hydrogen, completely (about 1 grain per 1,000 cubic feet) purified from sulfur, was passed over a nickel-aluminum-manganese on kieselguhr catalyst at 190 to 210° C and atmospheric pressure. The estimated cost of the motor fuel was 22 pfennigs per kilogram. At the time the first plant was erected, the following problems had to be solved if large-scale operation was to be successful: [25] (1) prolongation of the life of the catalyst from 4 to 6 weeks to at least as many months; (2) cheap indus-

trial design of contact chambers and sulfur-elimination plant; (3) industrial processes for the recovery of rare metals and oxides in the purest form from the exhausted catalysts; (4) conversion of Fischer's primary product, "Kogasin," into marketable gasoline, since only the fraction boiling up to 140° C had enough anti-knock properties (without addition of tetraethyllead) to be sold as motor fuel; and (5) the preparation of cheap synthesis gas.

The laboratory research work leading to the solution of these problems will be outlined in subsequent sections of this chapter. Since no description of the engineering and development work at the various Fischer-Tropsch plants has been published, only a general outline of the industrial development can be given.

During 1935 and 1936 a number of general reviews of the process and of its industrial progress, particularly in Germany, were published.[26] At the end of 1936 the following plants, aggregating a total capacity of 145,000 metric tons of primary oils per annum, were completed or under construction: the Rheinpreussen Colliery at Homberg, 30,000 metric tons of primary products consisting of gasoline, Diesel oil, soft and hard paraffin wax, oils for the production of fatty acids, and for other chemical uses, from blast-furnace coke and coke-oven gas; [27] Ruhr Benzin A.-G. (sub-

22 Hartner-Seberich, R., and Koch, H., *ibid.*, 13, 308–10 (1932). Fischer, F., and Koch, H., *ibid.*, 13, 428–34 (1932). Koch, H., and Horn, O., *ibid.*, 13, 164–7 (1932).

23 Anon., *Iron & Coal Trades Rev.*, 129, 542 (1934) ; *Times* (London), Nov. 19, 1934 ; *Gas- u. Wasserfach*, 77, 798 (1934) ; *Chem. & Met. Eng.*, 41, 666 (1934) ; *Fuel Economist*, 9, 303 (1934).

24 Fischer, F., Koch, H., and Wiedeking, K., *Brennstoff-Chem.*, 15, 229–33 (1934). Fischer, F., *ibid.*, 16, 1–11 (1935). Thau, A., *Colliery Guardian*, 150, 335–7 (1935). Koch, H., *Glückauf*, 71, 85–90 (1935).

25 Martin, F., *Ind. Chemist*, 13, 320–6 (1937).

26 Hall, F. C., *Oil Gas J.*, 33, 81 (1935). Sinnatt, F. S., *Gas J.*, 212, 711 (1935). Koch, H., *Glückauf*, 71, 85–90 (1935). Gillet, A. C., *Rev. universelle mines*, 11, 180–4 (1935). Schlattmann, O., and Koppenberg, H., *3rd World Power Conf., Washington, D. C., Sept. 1936*, Sect. II, Paper 4–5, 20 pp. Fischer, F., *J. Inst. Fuel*, 10, 10–4 (1936). Hugel, C., *Ann. combustibles liquides*, 11, 719–33 (1936). Thau, A., *Coal Carbonization*, 2, 159–63 (1936). Muhlert, F., *Chaleur et ind.*, 17, 119–23 (1936). "Proteus," *Gas World*, 105, 362–3 (1936). Berthelot, C., and Hot, A., *Carburants de synthèse et de remplacement*, Dunod, Paris, 1936, 350 pp.

27 Anon., *Gas World*, 105, 120 (1936) ; *Gas J.*,

sidiary of Ruhrchemie) at Oberhausen-Holten,[28] and the Viktor Colliery at Castrop-Rauxel [29] each 30,000 tons of primary oil per year from coke; Braunkohle-Benzin A.-G., known as "Brabag," at Ruhrland, north of Dresden, 25,000 tons of primary oils using synthesis gas produced by the gasification of brown-coal briquets; [27] and Mitteldeutsche Treibstoff und Oel Werke (subsidiary of Wintershall A.-G.) at Kassel, 30,000 tons of primary oils using synthesis gas resulting from the gasification of brown coal.[30]

During 1937 and 1938, the capacity of these plants was increased so that the total yearly oil and gasoline output was raised to 300,000 tons; and toward the end of 1938 additional plants were under construction, which when completed would increase this output to a yearly total of 525,000 metric tons.[31]

In Japan, two plants have been reported: [32] one at Fushun having an annual output of 100,000 tons, and another belonging to the Mitsui Mining Company at Omudu (Kyushu), completed at the end of 1938, of 50,000 tons per year capacity. According to other reports, the Showa Steel Company was erecting a 200,000 tons per year plant, and two others of 30,000 tons per year were in process of construction, one by the Mitsui Mining Company at Miike and another by the Synthetic Fuel Company at Chinchou.[33] Some development work done in a semi-industrial-size plant was also reported.[33] Tests made

with 2.5-, 3.5-, and 5.5-centimeter catalyst tubes of 56-centimeter length immersed in an oil bath and containing a cobalt-copper-thorium-uranium-kieselguhr catalyst gave yields of 98, 78, and 40 cubic centimeters of oil per cubic meter of synthesis gas. These tests indicated that narrow tubes were preferable, but the conclusion is not clear cut because the space velocity varied greatly, since the throughput was maintained constant at 100 liters per hour for all the tests.

In France the Société Courrières-Kuhlmann had a Fischer-Tropsch plant of about 20,000 tons per year capacity at Harnes in the Pas de Calais district. This plant was brought into operation in June 1937 at only about half its full capacity.[34] In Great Britain an experimental plant with a capacity of about 150 gallons per day has been constructed to test the Robinson-Bindley process,[35] which differs from that of Fischer and Tropsch in several respects and particularly in that it operates with a higher carbon monoxide-to-hydrogen ratio. A smaller experimental plant of about 4-gallon-per-day capacity has been erected by the Fuel Research Board.[36] Experiments done in these experimental plants will be discussed in later sections of this chapter.

In 1939, Germany was reported [37] to have been producing at the rate of 500,000 tons per year of gasoline, Diesel oil, and paraffins by the Fischer-Tropsch process.

215. 482 (1936) ; *Colliery Guardian*, **153**, 419 (1936) ; *Chem. Age*, **35**, 187 (1936).

[28] Anon., *ibid.*, **35**, 367 (1936).

[29] Anon., *Colliery Guardian*, **153**, 380–1 (1936).

[30] Anon., *Chem. Trade J.*, **99**, 50 (1936).

[31] Wilke, G., *Chem. Fabrik*, **11**, 563–8 (1938). Anon., *Petroleum Press Service*, **5**, 301–4 (1938).

[32] Ruprecht, P., *Oel Kohle Erdoel Teer*, **14**, 83–5 (1938). Anon., *Chem. Age*, **39**, 391 (1938).

[33] Anon., *J. Fuel Soc., Japan*, **17**, 57 (1938), **18**, 7 (1939) ; *Chem. Ind.*, **62**, 580 (1939).

[34] Hirsch, E., *Mém. soc. ing. civils France*, **90**, 756–67 (1937) ; *Rev. carburants France*, **1**, 505–9 (1938). Anon., *Chem. Trade J.*, **100**, 212 (1937).

[35] Myddleton, W. W., *Chimie & industrie*, **37**, 863–4 (1937) ; *J. Inst. Fuel*, **11**, 477–84 (1938) ; *Colliery Guardian*, **157**, 286–90 (1938).

[36] Dept. Sci. Ind. Research (Brit.), *Fuel Research Board, Rept. for the Year Ended March, 1937*, pp. 142–7.

[37] Bristow, W. A., *Colliery Guardian*, **159**, 625–6 (1939).

The latest plant was operated on low-temperature coke, which had been found best for the water-gas process because of its high reactivity. In 1940, Underwood[38] wrote: "Over 1,000,000 tons of Fischer liquid per year are being produced in Germany at present by this process."

of solid paraffin (melting point 20 to 100° C). The gasoline fraction had a low octane number (about 40), and hence a part of the oil was cracked to increase this number. The Diesel oil fraction had a cetene number between 100 and 120, and it was therefore a desirable blending con-
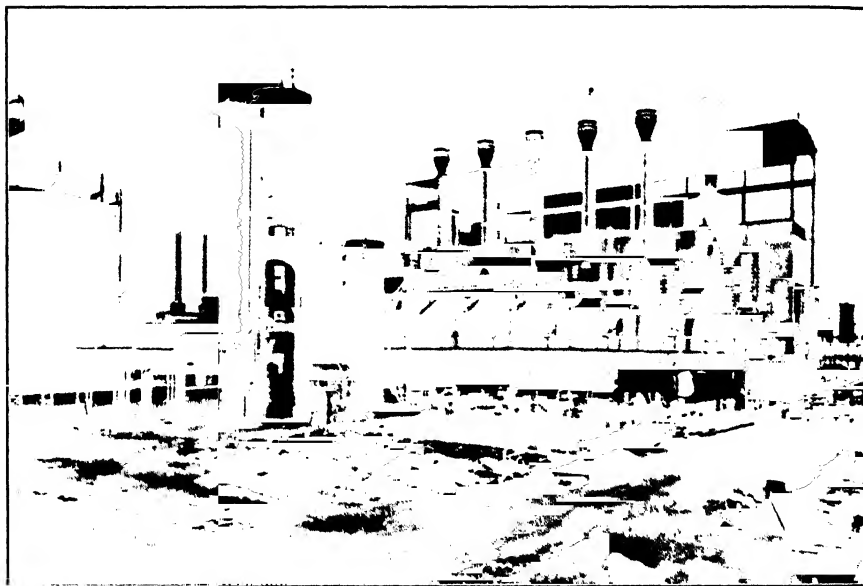
FIG. 1. Synthesis gas generators, Ruhrchemie plant.

Martin[25, 39] has given in several publications a general description of the German plants (see Figs. 1 to 7) and has presented some information on the nature of the products. The yield of primary product was reported to be about 125 grams per cubic meter of synthesis gas. This product included 8 percent of gaseous hydrocarbons, 60 percent gasoline (boiling to 200° C), 22 percent gas oil, and 10 percent

stituent for improving oils of low ignitibility. Excellent lubricating oils also could be synthesized from certain fractions of the primary product.[40]

The Fischer-Tropsch process is a remarkable one because of its great flexibility, both as regards raw materials and products obtainable. A variety of types of coke and coal as well as coke-oven gas and natural gas may be used as raw materials for synthesis gas production, and the proportion of gasoline and of other

38 Underwood, A. J. V., *Ind. Eng. Chem.*, **32**, 449–54 (1940).

39 Martin, F., *Oel, Kohle, Erdoel, Teer*, **13**, 691–7 (1937) ; *Chem. Fabrik*, **12**, 233–40 (1939).

40 *Koppers Rev.*, **2**, 99–139 (1937).
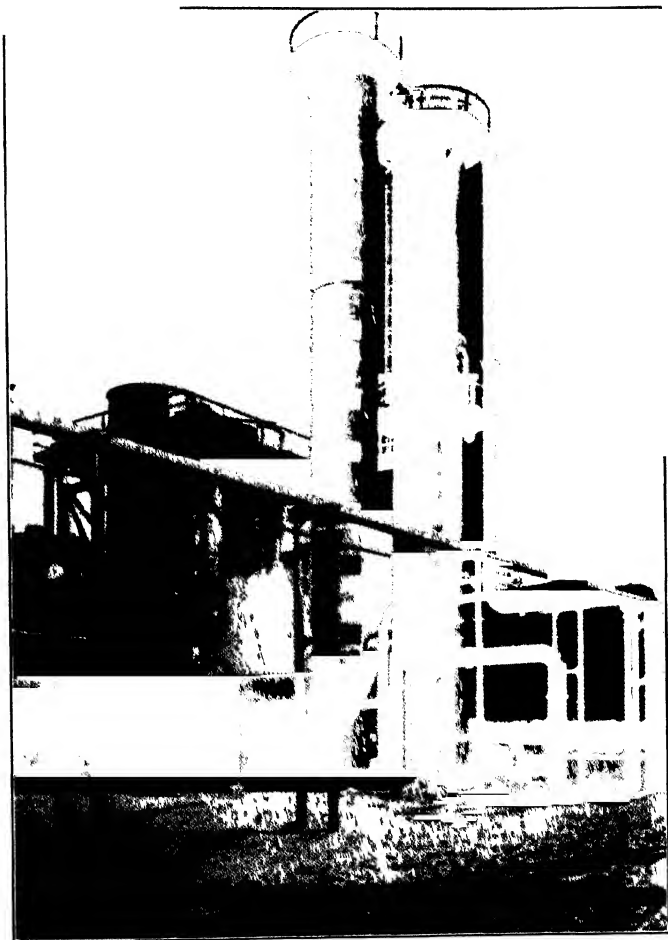
FIG 2. Water-gas shift converter, Ruhrchemie plant.

Fig. 3   Control floor of synthesis building containing contact chambers and control instruments Ruhrchemie plant

products may be varied considerably [41] Published reviews [41] of procedures and characteristics of products provide an adequate supply of general information concerning the Fischer-Tropsch process   In the following sections most of the available specific information will be presented

[41] Berthelot, C , *Génie civil*, **110**, 497–501 (1937), *Chimie & industrie*, **37**, 211–23 (1937), **40**, 434 60 (1938)   Berthelot C and Hot, A , *Technique et économie nouvelles des carburants de synthèse*, Dunod Paris 1937, 371 pp   Shatwell H G   *Colliery Guardian*, **155**, 1125–6 (1937) *J Inst Fuel* **11**, 209–17 (1938)   Thau A *Gas u Wasserfach*, **80**, 911–3 (1937) , *Z Ver deut Ing* , **83**, 906 (1939)   Fischer F *Chem Industries*, **40**, 33–5 (1937)   Anon *J Fuel Soc , Japan*, **16**, 10 1 (1937) , *Chem Age*, **38**, 164 (1938)   *Engineering*, **140**, 517 (1938) *Colliery Guardian*, **156**, 483–4 (1938)   Carr T P , *Gas World*, **109**, Coking Sect , 132–4 (1938)   Naphtali M *Refiner Natural Gasoline Mfr* , **17**, 47–51 (1938)   Dobse, H *Chem Fabrik*, **11**, 133 9 (1938)   Cawley, C M and Woodward, L A , *Petroleum Technology in 1938*, J Inst Petroleum Tech London, 1939 pp 393 409   Muhlert F , *Chaleur et Ind* , **20**, 355–60 (1939)   Applevard K C *S African Mining Eng J* , **50**, 585–7, 615–7 (1940)

[42] Ostermeier, L , *Gas u Wasserfach*, **81**, 52–7 (1938).

PRODUCTION OF SYNTHESIS GAS AND OF HYDROGEN

WATER-GAS PRODUCTION

The Fischer-Tropsch process or modifications thereof, such as the Robinson-Bindley, use as raw materials mixtures ranging in composition from 1 part of carbon monoxide to 1 or 2 parts of hydrogen Ostermeier [42] has given the following analy-

Fig 4. Top of contact chambers in synthesis building, Ruhrchemie plant.
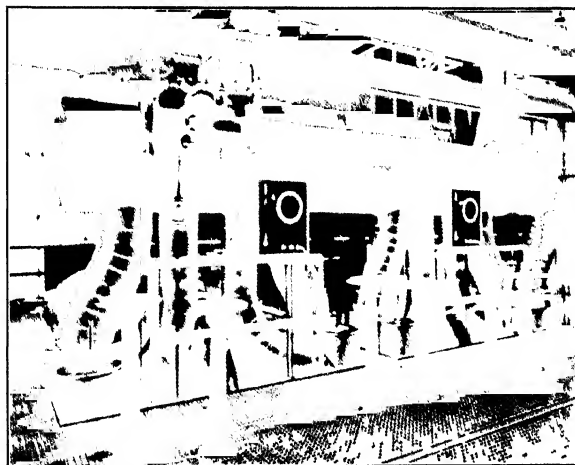
Fig 5 Vapor headers and fittings from contact chambers, Ruhrchemie plant
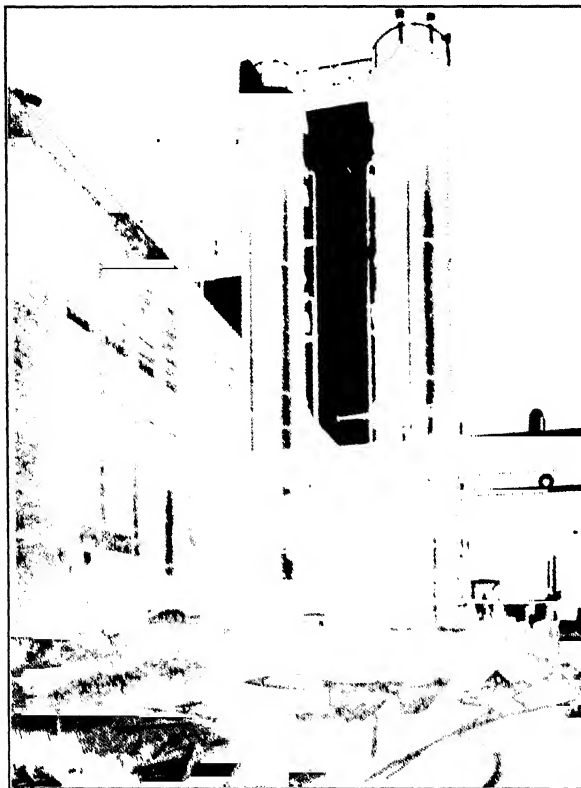
Fig. 6. Gas coolers for product condensation, Ruhrchemie plant.

sis as typical of the synthesis gas used on the commercial scale by Ruhrchemie A.-G. in Germany: 55.0 percent hydrogen, 27.5 percent carbon monoxide, 14.0 percent carbon dioxide, 0.6 percent methane, 2.7 percent nitrogen, and 0.2 percent oxygen. The principal source of mixtures of carbon monoxide and hydrogen is the reaction between steam (or carbon dioxide) and carbonaceous materials such as coal, coke, oil, coke-oven gas, or natural gas. In the direct hydrogenation of coal (see Chapter 38) excessive compression costs are avoided by keeping the purity of the hydrogen up to at least 92 percent. The Fischer-Tropsch process, however, can be satisfactorily operated with the content of inerts as high as 10 to 12 percent.

The average composition of water gas is 51 percent hydrogen, 40 percent carbon monoxide, 3 percent carbon dioxide, and 5 percent nitrogen. In practice, about 65 pounds of coke is consumed per 1,000 cubic feet of water gas produced. It is necessary to add to this coke consumption the amount necessary to produce the steam, of which about twice the theoretical amount is employed. (See Chapter 37.)
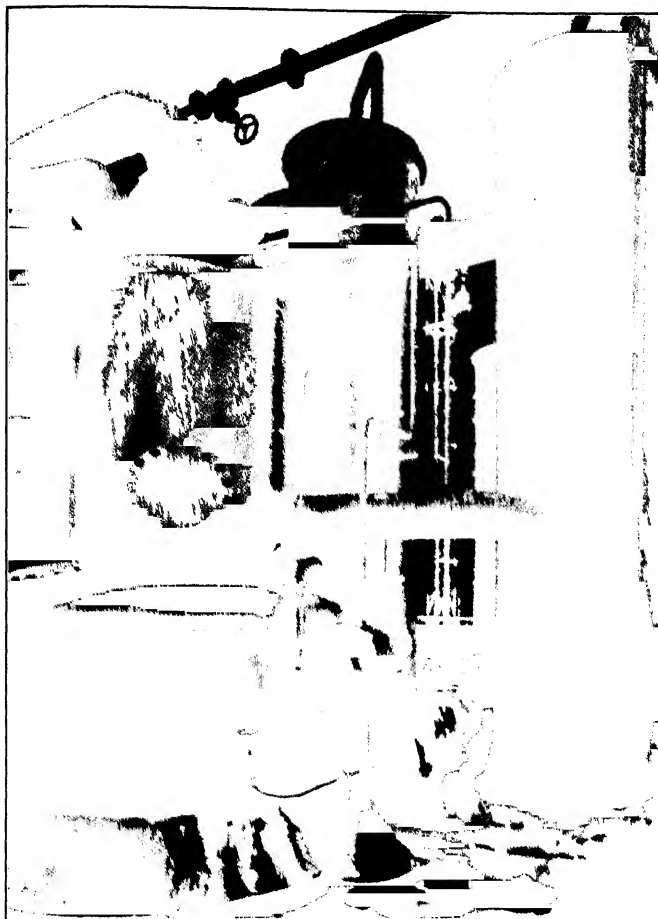
Fig 7 Active charcoal adsorbers Ruhrchemie plant

In the older water-gas generators periodic blasting with air is essential to maintain the operating temperature above 1,000° C These air-blasting operations are conducted at relatively high pressures and high space velocities so as to decrease the air-blast time to one-sixth to one-eighth of the steam blast and thereby reduce the heat losses At Belle, W Va, the du Pont Company operates the largest plant in the western hemisphere for the production of water gas by the classical system of alternate blasting with air and steam[43] Until 1936, one of the largest installations of

[43] Anon Ind Eng Chem, News Ed, 16, 354 (1938)

water-gas generators in the world was that at Billingham, England. There were 21 generators, each of which produced 172,000 to 950,000 cubic feet of water gas per 24 hours from coke and steam. These generators were 8.8 to 16.3 feet in diameter (inside). The German firms Bamag and Didier-Werke in 1936 built generators used for continuous blasting. In the Didier generator heat is supplied to the outside wall and steam is continuously passed through the interior.

In the Winkler generator either lignite, coal, or a semicoke ¼ inch in size can be used as fuel. Figure 8 shows such a generator with auxiliary equipment. The
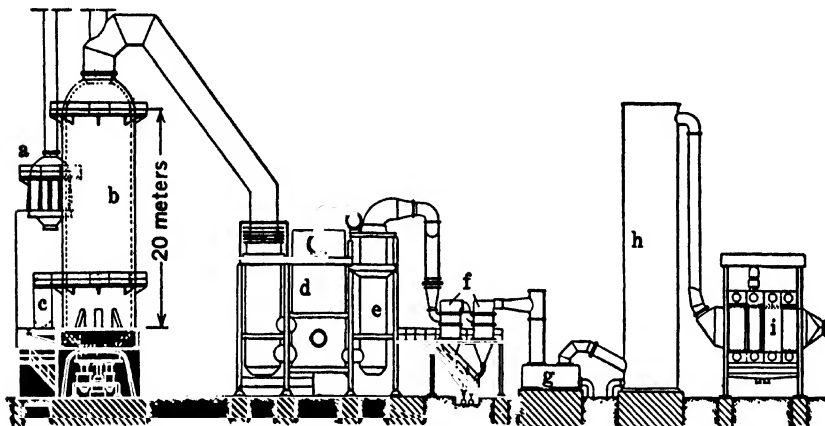
FIG. 8. Winkler water-gas generator operating with 0.6-millimeter (0.024-inch) coal.
(a) Gas generator for starting. (b) Gasification chamber. (c) Hopper for solid fuel. (d) Preheater, heated by hot water gas. (e) Heat exchanger. (f) Cyclone dust separator. (g) Liquid trap (h) Scrubber. (i) Electrostatic dust precipitator.

whose unit capacity was about 22 million cubic feet per day. The Bamag generators, which were of the Winkler model, were in service at Oppau and at Mersebourg. The Didier generators (also called "Gleichstrom") were in service at the Brabag plant at Ruhland in central Germany.[41] The Brabag plant had six generators, each with a capacity of about 900,000 cubic feet per hour. Brown-coal briquets were used to react with the steam. The outstanding characteristic of these generators is their continuous operation. Thus, in the Winkler generator 1 volume of oxygen plus 2 volumes of steam superheated to 375° C is

gasification chamber, b, is a cylinder 18 feet in diameter and 70 feet in height. The primary air plus steam, or the mixture of oxygen plus steam, is introduced in such fashion that the fuel bed is kept in turbulent agitation like a boiling liquid. In this way the fuel bed, which is about 5 feet thick, is heated rapidly and uniformly. The sintered ash particles settle on the grate, where they are cooled rapidly by the incoming oxygen (or air) and steam mixture. The solid fuel is fed through a hopper, c, into the bottom of the fuel bed. A rotating rabble (of brass, water-cooled) moves the ash toward a discharge port.

44 Anon., *Colliery Guardian*, **153**, 419 (1936).

In the gas-making cylinder, b, the gases must traverse a space 60 feet in height, which permits some separation of solids and a cooling of the gas, so that the exit temperature is 950° to 1,000° C. These gases are then given a preliminary treatment for dust removal followed by cooling in a spray tower and heat exchanger, e, further dedusting in a cyclone separator, f, scrubbing in the tower, h, and a final dust precipitation by an electrostatic machine, i.

Table I shows the composition of the product and the consumption of raw material.

TABLE I

PRODUCTS AND RAW-MATERIAL CONSUMPTION
IN WINKLER GENERATOR

Gas Composition	Oxygen + Steam	Oxygen + Air + Steam
	percent by volume	
CO_2	13 to 20	15.2
CO	47 to 36	32.9
H_2	39 to 41	29.7
CH_4	0.6 to 0.4	1.3
N_2	0.4 to 0.5	20.9
Raw-material consumption per 1,000 cubic feet of product		
Coke, pounds	40.9	33.0
Air, cubic feet		242
O_2 (98 percent) cubic feet	284	179
H_2O, pounds	19.	13.2

About seven of these large Winkler gas generators were in operation in Germany, and the one employed at Leuna produced 2,648,000 cubic feet of gas per hour.[45] The chief advantage of the Winkler machine is that it will function with a wide variety of finely divided fuels such as semicoke and lignite. In addition, its gas-generating capacity per square foot of generator surface is 5,000 to 10,000 cubic feet as compared with 1,500 cubic feet for the old-style water-gas machines.

The Didier[46] gas generator is a combi-

45 Anon., *Z. Ver. deut. Ing., 79*, 1094 (1935).
46 Didier-Werke A.-G., Fr. Pats. 834,716 (1938), 845,316 (1939); Ger. Pats. 669,434 (1938), 675,399 (1939); Brit. Pat. 499,018 (1939).

nation of a vertical retort and a water-gas generator, both being operated continuously. The bituminous coal or lignite moves downward from the hopper, A (Fig. 9), and the produced retort gas that flows up through the bed of hot coke has its methane content converted by pyrolysis
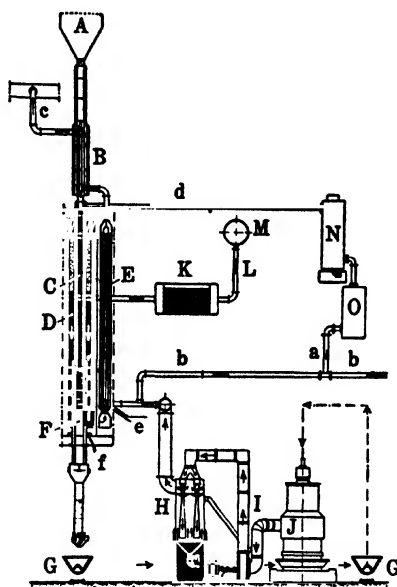
FIG. 9. Didier gas generator for CO + 2H₂ production.

(A) Hopper for solid fuel. (B) Drying zone. (C) Carbonization and gasification chamber. (D) Annulus for heating descending coal. (E) Predistillation zone. (F) Zone of water gas formation. (G) Coke receiver. (H) Water spray for dust removal from heating gas. (I) Cooler for heating gas. (J) Gas producer making heating gas. (K) Steam boiler operated on off-gas heat from annulus. (L, M) Synthesis gas to coolers and sulfur elimination plant. (N) Detarring condenser for predistillation gas. (O) Oil scrubber. (a) Predistillation gas freed from byproducts. (b) Predistillation gas to be used for heating carbonization chamber. (c) Stack for removal of gases from drying zone. (d) Predistillation gas going to detarring condenser. (e) Air for combustion. (f) Steam injector for water gas production.

and reaction with steam. The resulting gaseous product is a mixture of carbon monoxide and hydrogen suitable for the Fischer process. In the Didier gas generator unit there are six superposed zones. They are, in sequence, from the top down: (1) drying; (2) predistillation; (3) carbonization at high temperature; (4) conversion of gaseous hydrocarbons; (5) formation of water gas; and (6) cooling of coke. The first two zones are combined in one chamber, and the next three zones are combined in a cylindrical apparatus 15 feet high and 18 inches in diameter. A typical Didier installation consists of a large number of such units. From the first and second zones a gas containing all the water, some hydrogen sulfide, and hydrocarbons is obtained. After the ordinary purification, this gas is added to the producer gas made in J, and the combined fuel is used for heating the retort C. The water gas is drawn off at about the center of C. The carbonization gases travel up through the retort C and then down through the annulus D and are mixed with steam at F, the final gas product being drawn off at the center of C and sent to the heat exchanger K. Steam superheated to 400 to 500° C is injected at F.

The Didier generator uses ¼- to 1-inch bituminous coal or lignite briquets. The apparatus is designed to obtain enough methane (plus other gaseous hydrocarbons) so that subsequent pyrolysis with steam will yield the desired gas containing the desired ratio of carbon monoxide to hydrogen. Only such quantity of coke is produced as suffices for operating the gas producer, J, for heating the carbonization chambers. A part of the steam is produced by means of the sensible heat in the gases produced, and the remainder is obtained by the heat of reaction in the Fischer process. The composition of the product is: 9.4 percent carbon dioxide, 30.5 percent carbon monoxide, 56.5 percent hydrogen, 1.0 percent methane, 2.2 percent nitrogen, 0.2 percent oxygen, 0.2 percent C_nH_m in which the ratio of hydrogen to carbon monoxide is 1.95. The thermal efficiency when using lignite briquets is 75.5 percent.

An experimental gas generator similar in principle to the Didier machine has been described by Schmidt and Groh [47] and Jäppelt and Steinmann.[47] They used a simple masonry shaft, in the lower part of which a bundle of steel tubes was fixed. The fuel to be gasified was fed over a plate into the upper part of the shaft, which served as a drier, and a low-temperature retort. The coke then passed through the chromium-steel gasification tubes. The heat required for gasification was supplied partly in the form of superheated steam, which was blown into the lower part of the system, and partly by heat transmitted through the walls of the steel tubes, which were heated to about 1,100° C with waste gas. The heating gases were obtained from the combustion of coal or water gas. After heating the gasification tubes, these gases supplied heat for superheating the steam used for gasification and then went to the preheater for the heating gases and combustion air.

The Pintsch-Hillibrand [48] generator is similar to the Didier machine in that it has both a carbonization and a gasification zone. Lignite briquets pass countercurrent to a flow of a preheated mixture of steam, carbonization gas, and a fraction of the synthesis gas product.

47 Schmidt, I. R., and Groh, E., *Braunkohlenarch.*, No. 44, 50–3 (1936) ; *Oel, Kohle, Erdoel, Teer*, 12, 41–51 (1936). Jäppelt, A., and Steinmann, A., *Braunkohle*, 35, 353–7, 372–7 (1936).
48 Anon., *Génie civil*, 114, 88–91 (1939).

The Lurgi [49] process for the gasification of solid fuels using steam and oxygen under pressure has attracted considerable attention. It is a continuous process for producing a mixture of water gas and methane. The operating pressure is about 20 atmospheres. The generator consists of a refractory chamber surrounded by a water-filled annulus, the outer wall of which is the steel pressure retaining wall. The capacity per square foot of generator surface of the Lurgi machine is said to be about three times that of other types of water-gas generators.[48] The high operating pressure of the Lurgi generator favors the production of methane and of carbon dioxide. For Fischer-Tropsch synthesis gas neither of these constituents is desirable; but it is reported [50] that conditions can be so adjusted, particularly by adding carbon dioxide in appreciable amounts to the steam-oxygen mixture, as to minimize the production of methane and to produce a gas containing 62 percent hydrogen and 31 percent carbon monoxide.

The production of synthesis gas by various processes has been subjected to a technical analysis by Dolch,[19, 51] who concluded that, especially as regards the yield of gas, the oxygen-steam processes are far superior to those in which the heat required is obtained from the separate gasification of part of the fuel. He also claimed that carbonization and gasification in vertical ovens at atmospheric pressure

with oxygen-steam mixtures produces a gas containing little methane and consumes the least oxygen.

The use of coke-oven gas in the production of synthesis gas for the Fischer-Tropsch process has been included in several processes. One of these [52] produces a mixture of hydrogen and carbon monoxide in approximately the ratio 2 : 1 by alternately blowing a solid fuel in a gas producer with a mixture of steam and oxygen and a mixture of steam and coke-oven gas, and mixing the resulting gases in suitable proportions. Two other patents [53] also specify the blowing of coke-oven gas plus steam through the hot bed of a water-gas generator.

The production of hydrogen by the low-temperature fractionation of coke-oven gas has been reviewed in two papers.[54] The two main types of equipment are the Linde and the Claude, which differ only as regards the method of attaining the cooling effect. In the Linde (or Linde-Brown) process the Joule-Thomson effect is utilized for cooling. In the Claude process the cooling effect is obtained by causing the expanding gases, from a pressure of 30 to 40 atmospheres, to do external work, that is, to drive an engine, which has the effect of causing a rapid drop in temperature. In both processes all the coke-oven-gas constituents other than hydrogen are liquefied.

The gasification of low-temperature coke with steam seems to have been extensively practiced in Germany during 1932–9.[55]

49 Millett, H. C., *J. Inst. Fuel*, **10**, 15–21 (1936). Wilke, G., *Chem. Fabrik*, **11**, 563-8 (1938). Drawe, R., *Arch. Wärmewirts*, **19**, 201–3 (1938). Selden, R., *Ind. Eng. Chem*, *News Ed*, **16**, 535 (1938). Held, W., *Petroleum*, **35**, 435–7 (1939). Dolch, P., *Brennstoff-Chem.*, **20**, 101–11 (1939). Anon., *Trade and Engineering*, **44**, 17 (1939).

50 Metallgesellschaft A.-G., Brit. Pat. 504,529 (1939).

51 Dolch, P., *Feuerungstech.*, **27**, 1–5, 44–57, 103–8 (1939).

52 Studien- und Verwertungs-Gesellschaft m.b.H., Brit. Pat. 458,022 (1936).

53 Koppers, H., Brit. Pat. 466,737 (1937); U. S. Pat. 2,132,533 (1938).

54 Berthelot, C., *Génie civil*, **110**, 459–61 (1937). Brownlie, D., *Ind. Eng. Chem.*, **30**, 1139–46 (1938).

55 Anon., *Iron Coal Trades Rev.*, **139**, 285 (1939).

Wilke [56] described large-scale tests indicating that low-temperature coke of suitable quality could be gasified successfully in water-gas generators.

The production of mixtures of carbon monoxide and hydrogen by the oxidation of natural gas with oxygen, carbon dioxide, or steam is another important source of synthesis gas and of hydrogen. The partial oxidation of methane with oxygen to produce a mixture of carbon monoxide and hydrogen was studied by Liander,[57] who employed a nickel catalyst and temperatures up to 1,000° C. The partial oxidation of methane with oxygen at about 1,400° C was also studied by Fischer and Pichler.[58] They obtained mixtures of water gas and acetylene; thus, from a mixture of 2 parts of methane and 1 of oxygen with a contact time of about 0.01 second, a gas containing 54 percent hydrogen, 26 percent carbon monoxide, 9.4 percent acetylene, 4.8 percent methane, and 3.0 percent carbon dioxide was obtained. This product could be scrubbed free of acetylene (which would probably be used as the raw material for organic syntheses), and the residual gas could be used as synthesis gas for the Fischer-Tropsch processes.

Gluud [59] and his coworkers also experimented with partial oxidation of methane using a nickel-magnesium oxide catalyst at about 850° C. Several other experimenters [60] have studied the partial oxidation of methane and have found the reaction $2CH_4 + O_2 = 2CO + 4H_2$ to be complete at about 900° C when thoria- or silica-promoted nickel catalysts were used. Thus far none of these experiments has been carried into industrial-scale operation. However, the highly endothermic nature of the reaction of methane with steam or carbon dioxide and the relatively low cost of oxygen make it desirable to supply the heat of the reaction by partial combustion with oxygen.

A study of the production of carbon monoxide-hydrogen mixtures from methane plus steam and oxygen and from methane plus carbon dioxide and oxygen has been made by Natta and Pontelli,[61] in the temperature range 800 to 1,400° C. The ratio of carbon monoxide to hydrogen as a function of the initial composition of the reactant and temperature of the reaction was determined for the two ternary systems as well as for the quaternary system CH_4-CO_2-H_2O-O_2. Ogawa and his coworkers [62] have studied the partial oxidation of methane by activated iron oxide. A mixture of equal parts of ferric oxide and magnesium oxide was reduced by methane at 1,220° C, and, immediately after this reaction, the gaseous products were passed over a nickel-on-clay catalyst and emerged as 57 percent hydrogen, 28 percent carbon monoxide, 9 percent carbon dioxide, 3 percent methane, and 3 percent nitrogen. The process was intermittent, and it was necessary to use an air blast at 1,380° C to regenerate the ferric oxide. If the nickel catalyst was omitted, the methane content of the off-gas rose to about 13 percent.

56 Wilke, G., *Tech. Mitt. Krupp*, **5**, 44–9 (1937).

57 Liander, H., *Trans. Faraday Soc.*, **25**, 462–72 (1929).

58 Fischer, F., and Pichler, H., *Brennstoff-Chem.*, **11**, 501–10 (1930); Fr. Pat. 719,035 (1931).

59 Gluud, W., Keller, K., Klempt, W., Bestehorn, R., Brodkorb, F., Schröter, J., and Curland, E., *Ber. Ges. Kohlentech.*, **3**, 211–370 (1930).

60 Yoshikawa, K., *Bull. Chem. Soc. Japan*, **6**, 106–10 (1939). Padovani, C., and Franchetti, P., *Gior. chim. ind. applicata*, **15**, 429–32 (1933). Karzhavin, V. A., and Leibush, A. G., *J. Chem. Ind. (U.S.S.R.)*, **15**, No. 1, 34–8 (1934).

61 Natta, G., and Pontelli, R., *Chimica e industria (Italy)*, **19**, 177–82 (1937).

62 Ogawa, T., Matsui, A., Nagai, H., and Senoo, H., *J. Soc. Chem., Japan*, **43**, Suppl. Binding, 116–7 (1940).

Equilibrium relations [63] involved in the methane-steam reaction show that above 850° C, when an excess of steam is avoided, the reaction is almost entirely confined to $CH_4 + H_2O = CO + 3H_2$; and with excess of steam present at a temperature of about 750° C the reaction is mainly $CH_4 + 2H_2O = CO_2 + 4H_2$. In the absence of catalysts, the rate of reaction of methane with steam is slow, becoming appreciable only at temperatures higher than 1,300° C. Fischer and Tropsch [64] investigated the activity of a variety of catalysts for the reaction $CH_4 + CO_2 \rightarrow 2CO + 2H_2$. Copper, iron, molybdenum, and tungsten were found to have little or no catalytic activity at 850° C, whereas cobalt or nickel promoted with alumina were excellent catalysts.

Hawk, Golden, Storch, and Fieldner [65] found cobalt to be a much poorer catalyst than nickel for the methane-steam reaction at 900 to 1,000° C. These experimenters developed a small-scale intermittent process, first blasting the catalyst with a gas-air mixture, then injecting the reaction mixture into the catalyst bed. Catalysts of nickel deposited on a refractory mixture of alumina and clay were most satisfactory in respect of activity and durability. In the temperature range 900 to 1,000° C, nearly theoretical conversions were obtained.

A considerable number of catalysts have been tested by other experimenters. Nickel-thoria-magnesia and nickel-iron supported on kieselguhr were recommended for the reaction $CH_4 + H_2O = CO + 3H_2$ at about 800° C.[66] Nickel-alumina-magnesia on active carbon was suggested by Dansila and Piatkowski [67] for the reaction $CH_4 + 2H_2O = CO_2 + 4H_2$ at 650° C. Nickel-zinc oxide on kieselguhr or chamotte was very effective [68] in the reaction of propane and butane with steam at about 500° C to yield mainly a mixture of equal parts of carbon dioxide and hydrogen. Nickel-magnesia was recommended by Tsutsumi [69] for both the methane-steam and the water-gas shift reaction (see below). Sweeney and Spicer [70] patented a mixture of 25 percent nickel, 74 percent magnesia, and 1 percent boric acid as catalyst for the methane-steam reaction at 815 to 925° C. Ogura [71] studied the behavior of nickel-alumina on clay for the same reaction at about 600° C.

Semi-industrial-scale plant data have been presented by Karzhavin [72] for the conversion of methane to synthesis gas by means of an intermittent process very similar to that used by Hawk and his co-workers.[65] Hirsch [73] has discussed the operation of an automatically controlled full-scale plant for the methane-steam reaction; and Brownlie [54] has briefly described the industrial plants of the Standard Oil Company of New Jersey at Bayway, N. J., and at Baton Rouge, La. At these plants a temperature of 870° C was

[63] Randall, M., and Gerard, F. W., *Ind. Eng. Chem.*, **20**, 1335–40 (1928). Kubelka, P., and Wenzel, W., *Metallbörse*, **21**, 1227–8, 1275–6, 1372–3, 1421–2 (1921). Schmidt, J., and Neumann, B., *Z. Elektrochem.*, **38**, 925–34 (1932).

[64] Fischer, F., and Tropsch, H., *Brennstoff-Chem.*, **9**, 39–45 (1928).

[65] Hawk, C. O., Golden, P. L., Storch, H. H., and Fieldner, A. C., *Ind. Eng. Chem.*, **24**, 23–7 (1932).

[66] Klyukvin, N. A., and Klyukvina, S. S., *Natural Gases (U.S.S.R.)*, **1934**, No. 8, 52 8.

[67] Dansila, N., and Piatkowski, T., *Bull. sect. sci. acad. roumaine*, **19**, 11–27 (1937).

[68] Rakovskii, E. V., Burimova, O A., and Rakovskii, M. E., *Khim. Tverdogo Topliva*, **8**, 374–83 (1937).

[69] Tsutsumi, S., *J. Fuel Soc., Japan*, **17**, 24 8 (1938).

[70] Sweeney, W. J., and Spicer, W. E., U. S. Pat. 2,125,743 (1938).

[71] Ogura, T., and Huzimura, T., *J. Chem. Soc., Japan*, **60**, 139–48 (1939).

[72] Karzhavin, V. A., *Ind. Eng. Chem.*, **28**, 1042–4 (1936).

[73] Hirsch, E., *Mém. soc. ing. civils France*, **85**, 286–302 (1932).

used, and a mixture of carbon monoxide, carbon dioxide, and hydrogen was obtained from the methane-steam reaction. The use of nickel stampings as catalyst for the methane-steam reaction has been described by Storch and Fieldner,[74] who described the experimental plant (500 cubic feet of hydrogen per hour capacity) at the Central Experiment Station of the Bureau of Mines in Pittsburgh, Pa.

Experimenters have attempted to absorb continuously in the reaction zone the carbon dioxide produced by the reaction $CH_4 + 2H_2O = CO_2 + 4H_2$ so as to obtain virtually pure hydrogen.[59, 75] Ignited dolomite has served not only to absorb carbon dioxide but also to convert any carbon monoxide to the dioxide. However, regeneration of the calcium oxide by heating at 850 to 900° C destroys the activity of the nickel catalysts for operation at 500 to 600° C.

The British Fuel Research Board[76] has experimented with a combination of the production of water gas from coke and the Lane hydrogen process, which consists in alternate reduction and oxidation at 700 to 800° C of calcined spathic iron ore; the reduction is effected by water gas, and the oxidation of the reduced iron with steam produces hydrogen. In this combination the spathic iron ore replaces the checkered brickwork normally used in the tar-cracking chamber in the complete gasification of medium caking coal. The temperature of the ore is raised to 700 to 800° C by the hot gases produced during the burning of the blow gas, and the ore is reduced by passing through it the water gas produced during the up-run.

A new process for obtaining hydrogen from low-grade fuel was suggested by Chekin, Semenoff, and Galinker,[77] which consisted in mixing fine, waste coal with iron ore and heating at 850 to 900° C in a rotary furnace through which air is passed. The product, which consists of finely divided iron mixed with coal ash, passed to a second rotary furnace maintained at 500 to 700° C, into which steam was admitted The hydrogen obtained was fairly pure, only traces of carbon oxides and methane being present.

WATER-GAS SHIFT

The oxidation of the carbon monoxide in water gas with steam according to the reaction $CO + H_2O = CO_2 + H_2$ is extensively practiced as a step in the production of pure hydrogen. Equilibrium calculations[78] show that, to reduce the carbon monoxide content to about 0.1 percent when using 3 to 4 volumes of steam per volume of water gas, it is necessary to operate at temperatures not higher than about 350° C. White and Shultz[79] showed that catalysts made by the fusion and partial reduction with hydrogen of cobalt oxide effectively catalyze the water-gas shift reaction to equilibrium at temperatures as low as 283° C and space velocities of 1,800 volumes of water gas per volume of catalyst per hour. The addition of suitable promoters such as chromium oxide or copper suppressed the simultaneous for-

[74] Storch, H. H., and Fieldner, A. C., *Mech. Eng.*, **61**, 605–11 (1939).

[75] Karzhavin, V. A., *J. Chem. Ind.*, (*U.S.S.R.*), **1934**, No. 2, 31–3; *Trans. Chem. Eng. Cong.*, *World Power Conf.*, **1936**, Paper G-17. Zahn, O., *Chem.-Ztg.*, **61**, 298–9 (1937). Tropsch, H., U. S. Pat. 2,057,402 (1936).

[76] Dept. Sci. Ind. Research (*Brit.*), *Fuel Research Board, Rept. for the Year Ended March, 1937*, pp. 136–41, *1938*, pp. 184–5.

[77] Chekin, P. A., Semenoff, A. I., and Galinker, I. S., *Compt. rend. 15th congr. chim. ind.*, **1**, 410-4C (1935).

[78] Bryant, W. D., *Ind Eng. Chem.*, **23**, 1019 21 (1931). Ghosh, J. C., Chakravarty, K. M., and Bakshi, J. B., *Z. anorg. allgem. Chem.*, **217**, 277–83 (1934).

[79] White, E. C., and Shultz, J. F., *Ind. Eng. Chem.*, **26**, 95–7 (1934).

mation of methane. A cobalt catalyst containing about 38 percent of copper was shown to be particularly active, and a simple method for the preparation and regeneration of this catalyst has been given by Storch and Pinkel.[80] The cobalt-copper catalysts are sensitive to sulfur compounds, and hence the water-gas must be purified. Ivanovskiĭ and Braude[81] suggested the addition of a small amount of potassium dichromate to this catalyst.

Iron catalysts promoted by chromium and magnesium oxides are active at temperatures of 450 to 500° C and are quite resistant to sulfur poisoning.[82] The optimum ratio of Fe : Cr_2O_3 : MgO was found to be 1 : 1 : 0.03. Magnesia and zinc oxide promoted with a few percent of potassium oxide have been reported[83] to be effective catalysts at about 360° C. Schüssl has stated that a catalyst composed of active carbon and magnesia promotes the water-gas shift reaction at 350 to 420° C and 12 to 14 atmospheres pressure with but little methane formation.[84] This catalyst is not sensitive to sulfur poisons. Nickel catalysts promoted with a variety of nonreducible oxides have been tested for their activity in the water-gas shift reaction.[85] Nickel plus 10 percent magnesia was recommended.

SULFUR REMOVAL FROM SYNTHESIS GAS

For use in the Fischer-Tropsch process it is necessary to remove from synthesis gas the organic sulfur compounds until they are not present in excess of 0.2 gram per 100 cubic meters (about 1 grain per 1,000 cubic feet). This problem has been studied by Roelen and Roelen and Feisst,[86] who have recommended a multistage process in which the initial step is the removal of hydrogen sulfide by moist iron oxide. This is followed by decomposition of part of the organic sulfur compounds by the action of a mixture of sulfurized iron and alkali metal carbonate at 300 to 450° C, cooling, and removal of hydrogen sulfide by moist iron oxide. The last stage is the passage of the partly desulfurized gas at a temperature of 150 to 300° C over a mixture of iron oxide and a relatively large percentage of an alkali metal carbonate. Tsuneoka and Funasaka[87] also have found an iron oxide catalyst effective at 350° C and a space velocity of 330 volumes of gas per volume of catalyst per hour. They used the "red mud" obtained as a byproduct in the manufacture of aluminum; it was dried for 12 hours at 105° C and then crushed to 3- to 5-millimeter (⅛- to ¼-inch) granules.

Funasaka and Katayama[88] studied the influence of various promoters for the iron oxide catalysts. They found that the addition of 10 percent each of sodium hydroxide and thoria greatly improved the iron oxide catalyst. These investigators showed that a 7 : 3 mixture of Luxmasse (technical iron oxide) and diatomaceous earth with 30 percent sodium hydroxide at

[80] Storch, H. H., and Pinkel, I. I., *Ind. Eng. Chem.*, **29**, 715 (1937).

[81] Ivanovskiĭ, F. P., and Braude, G. E., *J. Chem. Ind. (U.S.S.R.)*, **15**, 14 9 (1937).

[82] Kurokawa, M., and Takenaka, Y., *J. Soc. Chem. Ind., Japan*, **40**, Suppl. Binding, 347 (1937).

[83] Natta, G., and Rigamoti, R., *Chimica e industria (Italy)*, **18**, 623–30 (1936).

[84] Schüssl, F., *Gas- u. Wasserfach*, **82**, 359–62 (1939).

[85] Tsutsumi, S., *J. Chem. Soc., Japan*, **58**, 379

80 (1937), **60**, 311–3 (1939). Chakravarty, K. M., *Science and Culture*, **3**, 396 (1938).

[86] Roelen, O., *Brennstoff-Chem.*, **12**, 305–12 (1931). Roelen, O., and Feisst, W., Ger. Pat. 651,462 (1937); U. S. Pats. 2,110,240–1 (1938).

[87] Tsuneoka, S., and Funasaka, W., *J. Soc. Chem. Ind., Japan*, **41**, Suppl. Binding, 43–51 (1938).

[88] Funasaka, W., and Katayama, I., *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **35**, 32–46 (1938).

350° C reduced the sulfur to 0.07 gram per 100 cubic meters (after subsequent hydrogen sulfide removal). Funasaka [89] claimed to have developed satisfactory catalysts by the addition of 10 percent of copper or nickel hydroxides to Luxmasse containing 10 percent of sodium hydroxide. This catalyst when used at 200 to 250° C and at a space velocity per hour of about 250 was reported to reduce the sulfur content of synthesis gas to less than 0.2 gram per 100 cubic meters.

Griffith [90] studied the removal of organic sulfur by catalytic oxidation. A small quantity of oxygen (0.6 percent) was mixed with the gas and the mixture passed over a nickel catalyst prepared by deposition of nickel hydroxide on china clay. The product, after removal of sulfur dioxide and hydrogen sulfide, contained about 10 grains of organic sulfur per 1,000 cubic feet. This sulfur content is too high for the Fischer-Tropsch process but may be lowered, perhaps, by the discovery of a more efficient catalyst.

Another method of removing organic sulfur compounds from gases containing hydrogen is by catalytic reduction to hydrogen sulfide which may then be removed by moist iron oxide in the usual manner. This method offers the possibility of using much higher space velocities than possible with the activated iron oxide-alkali catalysts. The British Fuel Research Board has reported some preliminary results of tests of this method in which a supported uranium-cerium catalyst developed by Huff and Logan was used. [91] The catalyst contained uranium and cerium in the ratio of

4 : 1 by weight and was prepared by precipitation by ammonia of the hydroxides onto pumice from a solution of the nitrates. The dried catalyst, before reduction, contained two-thirds of its weight of pumice; it was reduced before use with pure hydrogen for 2 hours at 450° C, and was then run with sulfur-containing gas for 1 hour at the same temperature before measurements were begun. The subsequent performance was much impaired if the catalyst was allowed to cool down in hydrogen during this initial reduction and pretreatment with sulfur-containing gas.

The experiments with carbon bisulfide and thiophene in hydrogen were carried out with a catalyst volume of 10 cubic centimeters. The apparatus included a constant-temperature entrainment system whereby a definite amount of organic sulfur compound could be introduced into the ingoing gas stream. The space velocity per hour was 5,700, and the temperature 450° C. The hydrogen sulfide formed in the catalyst chamber was removed from the effluent gas by passage through alkaline potassium ferrocyanide solution, and the unchanged organic sulfur was determined by combustion. Table II contains the results of a run on the removal of carbon bisulfide entrained in hydrogen in amounts comparable with those of organic sulfur commonly encountered in water gas. The catalyst ages in the second column refer to times half-way through the corresponding effluent sulfur determinations, each of which requires 2 hours. At first the catalyst was used only during the daytime, being allowed to cool down over night in pure hydrogen and raised in 1 hour to reaction temperature the next morning before admission of the carbon bisulfide. From the results obtained in two subsequent periods of continuous running (see Table II) it appears that the cooling and

[89] Funasaka, W., *ibid.*, **37**, 323–7 (1940).

[90] Griffith, R. H., *Gas World*, **107**, 381–3 (1937).

[91] *Dept. Sci. Ind. Research* (*Brit.*), *Fuel Research Board, Rept. for the Year Ended March, 1939*, pp. 164–7. Huff, W. J., and Logan, L., *Proc. Am. Gas Assoc.*, **1936**, 724.

TABLE II

CATALYTIC REMOVAL OF CARBON DISULFIDE FROM HYDROGEN [91]

Mode of Running	Age of Catalyst	Sulfur as Carbon Disulfide	
		Ingoing	Effluent
	hours of running	grams per 100 cubic meters	
Intermittent	2	29.0	0.05
(27 hours)	9	29.0	0.05
	17	29.0	0.05
	24	29.0	0.05
	26	29.0	0.06
Continuous	29	45.0	0.05
(72 hours)	52	45.0	0.12
	62	45.0	0.28
	76	45.0	0.31
	98	45.0	0.38
Continuous	101	64.0	0.09
(96 hours)	125	64.0	0.19
	173	64.0	0.30
	194	64.0	0.30

TABLE III

CATALYTIC REMOVAL OF THIOPHENE FROM HYDROGEN [91]

Mode of Running	Age of Catalyst	Sulfur as Thiophene	
		Ingoing	Effluent
	hours of running	grams per 100 cubic meters	
Intermittent	3	11.7	0.89
(15 hours)	7	11.7	0.92
	10	11.7	1.07
	14	11.7	1.13
Continuous	18	11.7	1.36
(28 hours)	42	11.7	1.70
Continuous	68	45.7	24.3
(26 hours)			
Intermittent	72	12.0	5.5
(12 hours)	78	12.0	6.2
	80	12.0	6.7
Catalyst treated with air for 3 hours at 450° C			
Intermittent	84	12.0	7.2
(7 hours)	87	12.0	8.6

reheating of the catalyst in pure hydrogen had a revivifying effect. The results show that the catalyst was very effective for the removal of carbon disulfide from hydrogen at the high throughput rate of 5,700 volumes per volume of catalyst per hour, but that a slight deterioration was apparent during continuous running. Blank experiments showed that the carbon disulfide content was unaffected when the gas was passed through the catalyst chamber at reaction temperature but in the absence of catalyst.

Analogous experiments were carried out with thiophene in place of carbon disulfide. As was expected, the thiophene was more difficult to decompose than carbon disulfide and caused a more rapid deterioration of the catalyst. The results of a run with thiophene are shown in Table III. The catalyst was first run on hydrogen containing 11.7 grams of sulfur (as thiophene) per 100 cubic meters. It was then run continuously with a higher thiophene content corresponding to 45.7 grams of sulfur per 100 cubic meters. As is seen from Table III, only about one-half of this increased

amount of thiophene was removed, and when a return was made to the original thiophene content it was found that the catalyst activity had been considerably impaired. This table also shows the results obtained after an unsuccessful attempt to revivify the catalyst by passing air over it at 450° C and then reducing it.

A run was carried out on the removal of carbon disulfide from a mixture of equal volumes of carbon monoxide and hydrogen, such as is encountered in water gas. The ingoing gas contained 80 grams of sulfur (as carbon disulfide) per 100 cubic meters, and after 22.5 hours' intermittent running the corresponding figure for the effluent gas was 2.3 grams. On changing over to hydrogen containing the same quantity of carbon disulfide the effluent figure became 0.38 gram per 100 cubic meters. Thus the performance of the catalyst was not so good when the concentration of hydrogen was reduced by admixture with carbon monoxide.

CATALYSTS

The most active catalysts for the synthesis of liquid and solid hydrocarbons from hydrogen and carbon monoxide are mixtures of nickel or cobalt, or both, with activating materials such as alumina, thoria, or other difficultly reducible metal oxides. Nickel plus 20 percent of manganese oxide and 4 to 8 percent of thoria, alumina, tungstic oxide, or uranium oxide, mixed with 1.25 times its weight of kieselguhr, yields 100 to 160 cubic centimeters of liquid hydrocarbons per cubic meter of synthesis gas per pass at a space velocity (volumes of gas per volume of catalyst per hour) of about 150 and at optimum temperatures in the range 185 to 210° C.[92]

Nickel catalysts have also been studied by Russian investigators.[93] Nickel catalysts are best prepared by the addition of alkali carbonates to solutions of the metal nitrates in which the kieselguhr is kept in suspension by mechanical agitation; the mixture is then filtered, washed, and dried. The presence of ammonia during the precipitation of nickel-manganese-alumina catalysts increases the yield in subsequent benzine synthesis and lowers the optimum reduction from 450 to 300–350° C.[94]

Cobalt catalysts containing 5 to 10 percent of copper, 4 to 12 percent of manganese oxide, and 4 to 12 percent of thoria, alumina, or uranium oxide mixed with 1.25 times their weight of kieselguhr yield[92] 120 to 170 cubic centimeters of liquid hydrocarbons per cubic meter of synthesis gas

per pass under the same conditions of space velocity and temperature as given above for nickel catalysts. The maximum theoretical yield is about 208 cubic centimeters per cubic meter of gas containing hydrogen and carbon monoxide in a 2 : 1 ratio. The use of cobalt catalysts generally results in a lower yield of methane and in a higher proportion of olefins in the liquid hydrocarbon product. About 50 percent of the cobalt may be replaced by nickel without appreciably affecting the important advantages of the cobalt catalysts.[95] The cobalt catalysts may be prepared by impregnation of kieselguhr with the metal nitrates and subsequent decomposition by roasting; their activity when thus prepared is about the same as when they are produced by precipitation from aqueous solutions.[96] It appears, however, that the precipitation method is preferable for the preparation of nickel catalysts.[97]

Fischer and his coworkers[98] have used a cobalt-copper-thoria-kieselguhr catalyst in most of their experiments. Tsutsumi[99] reported that a precipitated catalyst containing equal parts of cobalt and nickel without the addition of promoters such as thoria or alumina was a very poor one for the hydrocarbon synthesis. He stated that his most active catalyst was a mixture of equal parts of nickel and cobalt plus 20 percent manganese oxide, 20 percent uranium

92 Fujimura, K., and Tsuneoka, S., *J. Soc. Chem. Ind., Japan*, **36,** Suppl. Binding, 119–21, 413–6 (1933). Kita, S., *J. Fuel Soc., Japan*, **16,** 60–2 (1937). Tsutsumi, S., *ibid.*, **16,** 55–60 (1937).

93 Klyukvin, N. A., and Vol'nov, Y. N., *Khim. Tverdogo Topliva*, **4,** 355–62 (1933). Rapoport, I. B., Blyudov, A. P., Shevyakova, L., and Frantzuz, E., *ibid.*, **6,** 221–35 (1935).

94 Fischer, F., and Meyer, K., *Brennstoff-Chem.*, **14,** 47–50, 64–7, 86–9 (1933).

95 Tsuneoka, S., and Murata, Y., *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **34,** 280–300 (1938) ; *J. Soc. Chem. Ind., Japan*, **41,** Suppl. Binding, 52–7 (1938).

96 Tsutsumi, S., *Sci. Papers Inst. Phys. Chem Research (Tokyo)*, **35,** 481–6 (1939) ; **36,** 47–52 (1939).

97 Tsutsumi, S., *ibid.*, **36,** 251–61 (1939).

98 Koch, H., *Glückauf*, **71,** 85–90 (1935). Pichler, H., *Z. Ver. deut. Ing.*, **79,** 883–5 (1935) ; *Coal Carbonisation*, **1,** 101–3 (1935).

99 Tsutsumi, S., *J. Fuel Soc., Japan*, **14,** 110–6 (1935) ; *J. Chem. Soc., Japan*, **58,** 996–1006 (1937) ; *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **35,** 435–6 (1939), **36,** 335–43 (1939).

oxide, and 125 percent of kieselguhr (the percentages are based on the amount of nickel plus cobalt present). Tsutsumi [99] also found that the best ratio of catalyst to kieselguhr was in the range 1 : 1 to 2 : 1. Katayama and his coworkers [100] reported that the activity of a cobalt-nickel (1 : 1)-manganese-uranium-thorium oxides catalyst was increased by approximately 10 percent if it was oxidized at about 20° C by a slow stream (space velocity per hour of about 150) of air before its final reduction.

Another method of preparing active nickel and cobalt catalysts was invented by Raney.[101] Alloys of nickel or cobalt or both with silicon or aluminum are prepared by fusion of the constituents in an induction furnace. The silicon or aluminum is subsequently dissolved by aqueous caustic soda solution, leaving a "skeleton" of nickel or cobalt, which is a highly porous, catalytically active material. Fischer and Meyer [102] found that the use of silicon yielded catalysts of higher activity than those obtained from aluminum alloys; that the optimum ratio of nickel to cobalt was 1 : 1, and that the presence of small amounts of copper or manganese was undesirable. The catalyst prepared from nickel, cobalt, and silicon in the ratio of 1 : 1 : 2 was very dense with an apparent specific gravity of about 4.5 and yielded about 20 percent less liquid product in the hydrocarbon synthesis than was obtained from the same weight of nickel plus cobalt

in the form of the precipitated catalysts described above.[92] The precipitated catalysts deteriorated more slowly than the "skeleton" alloy catalysts, which, however, were better heat conductors. Since the reaction is markedly exothermic (about one-fourth of the heat of complete combustion is evolved) the improved heat conductivity would result in a lower plant-installation cost with alloy catalysts.

Attempts are being made to solve the heat-transfer problem by conducting the synthesis in a liquid medium in which the catalyst is suspended.[103] The heat of vaporization of the liquid removes heat rapidly from the catalyst surfaces. The disadvantages of the liquid medium are the difficulty of removing the products of the reaction and the larger space requirements. A procedure [104] designed to facilitate removal of the reaction product is to pass the preheated synthesis gas into a 50-bubble tray tower at the rate of 1,000 cubic feet per hour. A catalyst suspension containing about ¾ pound of finely divided nickel catalyst activated with magnesium and aluminum oxides suspended in 1 gallon of sulfur-free paraffin wax is charged through the tower at the rate of 300 gallons per hour. The reaction produces about 1 gallon of liquid hydrocarbons for each 1,000 cubic feet of gas charged.

The heat-transfer problem, when operating in a gaseous medium, is solved by the use of very narrow layers of catalyst and the heat of vaporization of water as the cooling mechanism, the water being contained in cooling jackets under 10 to 15

[100] Katayama, I., Murata, Y., Koide, H., and Tsuneoka, S., *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **34**, 1181–95 (1938) ; *J. Soc. Chem. Ind., Japan*, **41**, Suppl. Binding, 393–9 (1938).

[101] Raney, M., U. S. Pats. 1,563,587 (1925), 1,628,190 (1927), 1,915,473 (1933) ; *J. Am. Chem. Soc.*, **54**, 4116–7 (1932).

[102] Fischer, F., and Meyer, K., *Brennstoff-Chem.*, **15**, 84–93 (1934).

[103] I. G. Farbenindustrie A.-G., Brit. Pats. 449,274 (1936), 468,434 (1937), 516,352, 516,-403 (1939) ; U. S. Pat. 2,159,077 (1939). Fischer, F., and Pichler, H., *Brennstoff-Chem.*, **20**, 247–50 (1939).

[104] Standard Oil Development Co., Brit. Pat. 496,159 (1938).

atmospheres pressure. The catalyst depth is usually about 10 millimeters.[105]

Tsuneoka and his coworkers [106, 107] made a detailed study of the behavior of alloy catalysts for the Fischer-Tropsch hydrocarbon synthesis. In addition to confirming the results of Fischer and his coworkers,[102] the Japanese investigators studied the effects of particle size, bulk density of catalyst, pretreatment with hydrogen, and the material used for the construction of the reaction tube. They found that the optimum particle size for a space velocity of about 100 with a nickel-cobalt (1 : 1) catalyst prepared from the alloy nickel-cobalt-silicon (1 : 1 : 2) was 1 to 4 millimeters. The yield of liquid hydrocarbons was about 130 cubic centimeters (93 grams) per cubic meter of synthesis gas. The efficiency of the catalyst at constant gas input for a given amount of catalyst diminished when the free space exceeded or fell below a certain optimum value, which varied with the diameter of the reaction tube. Thus, for 10 grams of nickel-cobalt (1 : 1) catalyst and 4 liters per hour of synthesis gas the optimum length (L) for 13-millimeter tubing was about 30 centimeters; for 20-millimeter tubing L was 50 centimeters. If the length was shorter than the

optimum, the average molecular weight of the liquid hydrocarbon product decreased, and more gaseous hydrocarbons were produced. This effect was presumably due to the existence of higher local temperatures when the catalyst was packed into a smaller space. If the free space exceeded the optimum value, a lower yield per pass was obtained owing to "channeling" of the gas.

At constant gas input, tube diameter, and bulk density (grams of catalyst per cubic centimeter), and with varying quantities of catalyst (that is, varying space velocities), a limiting value was reached that depended on other reaction conditions. A further increase in the quantity of the nickel-cobalt catalyst (decrease in space velocity) did not influence the yield of liquid hydrocarbons but increased the yield of carbon dioxide and gaseous hydrocarbons. With less than the limiting amount of catalyst (that is, at higher space velocities) the liquid product was of lower molecular weight and also it contained more olefins. For a tube diameter of 8 millimeters, a bulk density of catalyst corresponding to 10 grams per 18 centimeters of tube length, and with a gas input of 4 liters per hour the best yield obtained with 22 grams of a nickel-cobalt catalyst at 180° C was 127 cubic centimeters (91 grams) per cubic meter of synthesis gas.

Pretreatment with hydrogen is not essential for the nickel-cobalt catalyst but appears to be desirable for the nickel catalyst obtained from a nickel-aluminum alloy. The latter catalyst, as well as those obtained from alloys of nickel with silicon, with manganese and silicon, and with iron and aluminum, are markedly inferior to the nickel-cobalt catalyst prepared from a nickel-cobalt-silicon alloy. The catalyst obtained from a nickel-cobalt-magnesium alloy is a very poor one; examination [107]

[105] Mannesmannröhren-Werke and Ruhrchemie A.-G., Brit. Pat. 464,242 (1937). I. G. Farbenindustrie A.-G., Brit. Pat. 469,618 (1937). Dorndorf, H., Kelting, M., and Tramm, H., U. S. Pat. 2,148,545 (1939). Ruhrchemie A.-G., Brit. Pat. 502,771 (1939).

[106] Tsuneoka, S., *J. Soc. Chem. Ind., Japan,* **37**, Suppl. Binding, 738–44 (1934). Tsuneoka, S., and Murata, Y., *ibid.,* **38**, Suppl. Binding, 199–212 (1935), **39**, Suppl. Binding, 267–78 (1936), **40**, Suppl. Binding, 438–49 (1937); *Sci. Papers Inst. Phys. Chem. Research (Tokyo),* **30**, 1–29 (1936), **33**, 305–32 (1937). Murata, Y., Tsuneoka, S., and Ishikawa, S., *J. Soc. Chem. Ind., Japan,* **39**, Suppl. Binding, 294–8, 325–33 (1936); *Sci. Papers Inst. Phys. Chem. Research (Tokyo),* **30**, 30–59 (1936).

[107] Tsuneoka, S., and Kuroda, R., *ibid.,* **33**, 333–8 (1937); *J. Soc. Chem. Ind., Japan,* **40**, Suppl. Binding, 449–54 (1937).

of polished and etched sections under the microscope indicate a much coarser crystal structure for it than for the nickel-cobalt-silicon alloy. Some data on the activity of nickel and cobalt catalysts obtained from nickel-aluminum, cobalt-aluminum, and cobalt-silicon alloys have been presented by Rapoport and Polozhintseva.[108]

The relatively high cost of cobalt and nickel has prompted continuous research on the development of iron catalysts for the hydrocarbon synthesis. Decarrière and Anthéaume [109] have claimed to have improved on the Fischer and Tropsch [10] iron-copper catalyst by using less copper. However, Kodama and Fujimura,[110] who studied iron-copper catalysts with the ratios 1 : 2, 1 : 1, 3 : 1 and 5 : 1, could find little, if any, difference in the catalytic activity of these four mixtures. They also found that an iron-copper (1 : 1) catalyst containing 0.5 percent of alkali was active for a considerably longer time than those containing more alkali.

X-ray studies [111] have shown that all active iron-copper precipitated catalysts contain magnetic iron oxide, Fe_3O_4 When sharply defined X-ray lines were obtained, the catalytic activity was least, owing to the presence of many large crystals. The active catalysts were found to have only weak magnetic susceptibility before the Curie point is reached. For a thermomagnetic study, Lefebvre and LeClerc [112] prepared two iron catalysts: one was precipitated from a solution of ferric nitrate by means of ammonia; and the other was similarly precipitated, but 1 percent of potassium carbonate was added to the catalyst. The former exhibited only one Curie point at 575° C corresponding to magnetic iron oxide, and yielded per cubic meter of synthesis gas 25 grams (35 cubic centimeters) of liquid hydrocarbons, which boiled almost entirely in the gasoline range (that is, about 200° C end point). The latter catalyst, containing 1 percent potassium carbonate, possessed two Curie points, the magnetic iron oxide one at 575° C and the other at 250° C, corresponding to a solid solution of potassium ferrite ($KFeO_2$) in ferric oxide. This catalyst yielded, per cubic meter of synthesis gas, 45 grams of liquid hydrocarbons, of which 20 grams was gasoline, 15 grams solid paraffin, and 25 grams oil boiling above 200° C. Subsequently LeClerc and Lefebvre [113] showed that the enhanced activity obtained by the addition of alkali carbonates to cubic Fe_2O_3 is due to the stabilization of this crystal form and prevention of transition to magnetic iron oxide, which is a much less active catalyst. This view is supported by LeClerc's measurements of the magnetic properties of the materials. The presence of alkali is indispensable for the formation of cubical ferric oxide; in the absence of alkali only magnetite is stable. The function of small quantities of other metals such as copper, which are known to be desirable constituents of iron catalysts, is to facilitate the reduction step that terminates the preparation of the catalyst and to favor the adsorption of a certain amount of alkali salt during the preparation of the catalyst, thereby aiding indirectly in the formation of cubical ferric oxide.

108 Rapoport, I. B., and Polozhintseva, E., *Khim. Tverdogo Topliva*, **9**, 64–70 (1938).

109 Decarrière, E. and Anthéaume, I., *Compt. rend.*, **196**, 1889–90 (1933).

110 Kodama, S., and Fujimura, K., *Sci. Paper Inst. Phys. Chem. Research (Tokyo)*, **29**, 272-84 (1936).

111 Anthéaume, I., Decarrière, E., and Réant, R., *Chimie & industrie*, **31**, 421–3 (1934).

112 Lefebvre, H., and LeClerc, G., *Compt. rend.*, **203**, 1378–80 (1936).

113 LeClerc, G., *Compt. rend.*, **207**, 1099–101 (1938). Lefebvre, H., and LeClerc, G., *Congr. chim. ind., Compt. rend., 18me congr., Nancy, Sept.-Oct. 1938*, 725–30.

Ghosh and Sen [114] prepared some iron-copper catalyst containing 0.5 percent potassium carbonate and small amounts of nickel and rare-earth oxides by impregnation of such quantities of asbestos with the metal nitrates that 50 percent of asbestos was present in the final catalyst. Passing 0.65 liter of synthesis gas per hour over 5 grams of each catalyst yielded 30 grams of liquid hydrocarbons per cubic meter for Fe-Cu-Ni, 4 : 1 : 0.01; 45 grams for Fe-Cu-Ni, 4 : 1 : 0.02; and 80 grams for Fe-Cu-Ni-CeO_2-ThO_2, 4 : 1 : 0.05 : 0.001 : 0.006. Tsuneoka and his coworkers [115] have also studied the preparation of iron-copper catalysts. Two catalysts, the one containing iron, copper, kieselguhr, and potassium carbonate in the ratio 4 : 1 : 5 : 0.08 and the other 0.08 part of manganese in addition to the same constituents as in the former catalyst, were prepared by mixing solutions of the nitrates with unpurified kieselguhr and precipitating with a solution of an equivalent amount of alkali carbonate. The precipitate, after filtration and washing, was impregnated with a small amount of potassium carbonate, air dried at 100° C, and pulverized. The yields were 83 and 88 cubic centimeters of liquid hydrocarbons, respectively, per cubic meter of a gas containing equal parts of hydrogen and carbon monoxide when 3.8 liters per hour per 4 grams of iron was employed at 250° C. The oxygen appeared entirely as carbon dioxide rather than as water, which is the main oxygen-containing product of cobalt and nickel catalysts. The optimum amounts of copper and potassium carbonate for this catalyst were found to be 20 to 40 percent and 2 to 3 percent, respectively. The addition of 5 percent of nickel or cobalt enhanced the activity for synthesis gas, but was undesirable for gas containing equal parts of hydrogen and carbon monoxide. Water formation was observed when the catalyst contained more than 2.5 percent of nickel. The addition of thoria, urania, etc., to an iron catalyst containing 10 percent of nickel did not affect its activity appreciably.

The I. G. Farbenindustrie A.-G. has reported that partial sintering of a precipitated iron-alumina catalyst by reduction at 850° C enhances its activity for the synthesis of liquid hydrocarbons.[116] Troitskii [117] recommended fusion of metallic iron or magnetic ore with potash or alumina or other activators in a stream of oxygen. Just before the melt solidified, a powder of the same composition, made under the same conditions, was added. Similarly prepared cobalt or nickel catalysts also were recommended. The I. G. Farbenindustrie A.-G. also recommended the production of catalysts of the iron group by decomposition of a carbonyl compound of the metal at such a temperature above 500° C but below the melting point of the metal, and for such a length of time, as produces at least partial sintering of the metal.[118] Thus, for example, iron powder that has been obtained by thermal decomposition of iron carbonyl was pressed into pills and heated at 850° C in the presence of hydrogen for several hours, whereby the pills sintered to a density of about 7. With synthesis gas at 320° C and 15 atmospheres pressure a "very good" yield of

114 Ghosh, J. C., and Sen, S., *J. Indian Chem. Soc.*, **12**, 53–62 (1935).

115 Tsuneoka, S., Murata, Y., and Makino, S., *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **35**, 330–47 (1939) ; *J. Soc. Chem. Ind., Japan*, **42**, Suppl. Binding, 107–14 (1939). Murata, Y., Makino, S., and Tsuneoka, S., *ibid.*, **42**, Suppl. Binding, 114–21 (1939) ; *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **35**, 848–55 (1939).

116 I. G. Farbenindustrie A.-G., Brit. Pats. 473,932, 474,448 (1937), 496,880 (1938).

117 Troitskiĭ, K. V., Russian Pat. 54,392 (1939) ; *Oel u. Kohle*, **36**, 73 (1940).

118 I. G. Farbenindustrie A.-G., Brit. Pat. 490,-090 (1938).

liquid and solid hydrocarbons and only minor amounts of oxygenated compounds were obtained.

Ruthenium powder itself and a mixture thereof with 2 percent potassium carbonate has been tested as catalyst for the Fischer-Tropsch hydrocarbon synthesis. Liquid hydrocarbons were obtained at atmospheric pressure,[119] and at about 90 atmospheres the product was mainly solid paraffins.[120] At atmospheric pressure the yield of hydrocarbons was very low, but at the higher pressure 120 grams of 80 to 90 percent solid paraffin plus 10 to 20 percent of oil were obtained. The use of ruthenium catalysts at pressures up to 1,000 atmospheres will be described in a later section of this chapter.

Some attention has been given to the selection of suitable refractory supports for precipitated catalysts and for catalysts prepared by impregnation of the support with a solution of nitrates and subsequent roasting. In addition to kieselguhr and asbestos, mentioned above, magnesium carbonate [121] and several other compounds, namely, barium sulfate, silicon carbide, chromium oxide, aluminum oxide, and silicates,[122] have been recommended. The Ruhrchemie A.-G. also suggested heating certain carrier materials to incandescence so as to reduce their solubility in any acid reagents that might be employed for catalyst regeneration.[123]

All the catalysts used in the synthesis of higher hydrocarbons from hydrogen and carbon monoxide are very readily poisoned by sulfur compounds. Thus, the activity

of nickel-manganese-thoria and nickel-manganese-kieselguhr catalysts was reduced 50 percent by 17 and 135 milligrams, respectively, of hydrogen sulfide per gram of nickel. The reported tolerance for carbon bisulfide of the same catalysts is much larger than that for hydrogen sulfide.[124] A similar report of a large tolerance for organic sulfur as compared with hydrogen sulfide was given by King [125] for cobalt-thoria-kieselguhr (100 : 18 : 100) catalyst. King stated:

In our experiments, carbon disulfide was added to the process gas over a period of 4 days to an extent corresponding to 33 milligrams of sulfur per cubic centimeter of catalyst. The catalyst continued to synthesize oil at a high degree of conversion, but in order to maintain the efficiency it was necessary to raise the temperature progressively from 185 to 210° C. With the space velocity used (190 volumes per volume per hour) the degree of fouling corresponds to about 10 years' working at the concentration of sulfur (0.2 gram per cubic meter) usually accepted as the highest permissible.

Fujimura and his coworkers [124] reported also that the initial effect of small amounts of hydrogen sulfide was to increase the catalyst (nickel-manganese) activity. This was confirmed by Herington and Woodward [126] for cobalt-thoria-kieselguhr (100 : 18 : 100) catalysts. Hydrogen sulfide was mixed with the synthesis gas in small measured batches. No hydrogen sulfide was eliminated in the off-gas during the course of the sulfur-poisoning experiments. The results are given in Table IV.

The first additions of sulfur caused a marked increase in the yield of liquid hy-

119 Fischer, F., Bahr, T., and Meusel, A., Brennstoff-Chem., 16, 466–9 (1935).

120 Fischer, F., and Pichler, H., ibid., 20, 247–50 (1939).

121 Ruhrchemie A.-G., Brit. Pats. 498,007 (1938), 518,334 (1939).

122 Ruhrchemie A.-G., Fr. Pat. 819,701 (1937).

123 Ruhrchemie A.-G., Brit. Pat. 500,182 (1939).

124 Fujimura, K., Tsuneoka, S., and Kawamichi, K., J. Soc. Chem. Ind., Japan, 37, Suppl. Binding, 395–400 (1934).

125 King, J. G., J. Inst. Fuel, 11, 484–5 (1938). Myddleton, W. W., ibid., 11, 477–84 (1938).

126 Herington, E. F. G., and Woodward, L. A., Trans. Faraday Soc., 35, 958–67 (1939).

TABLE IV

Amount of Sulfur Added	Catalyst Temperature	Ratio of Hydrocarbon Yield to Corresponding Yield before Addition of Sulfur	
		Condensed Oil	Hydrocarbons in Off-Gas $C_{1.7}$
milligrams per gram of catalyst	°C		
0.00	183	1.0	1.0
0.67	183	2.3	1.0
3.50	183	2.1	0.8
7.94	183	...	0.5
7.94	195	2.0	1.3
13.4	195	1.5	...
33.5	207	1.2	2.1

drocarbons at constant reaction temperature. There was, however, an immediate falling off in the yield of gaseous hydrocarbons. The total hydrocarbon yield increased until more than 8.0 milligrams of sulfur had been added to each gram of catalyst. Further additions of hydrogen sulfide caused a drop in total hydrocarbon yield, but, as shown in Table IV, this could be offset by raising the reaction temperature rather more rapidly than would normally be necessary in the absence of hydrogen sulfide. The higher temperatures favor the production of lighter hydrocarbons, but even so, after the addition of as much as 33.5 milligrams of sulfur per gram of catalyst, the yield of liquid hydrocarbons was still 20 percent greater than before the addition of sulfur. Further additions of sulfur resulted in a continuous decrease in activity until complete poisoning was reached.

PRESSURE, DILUENTS, HYDROGEN-TO-CARBON MONOXIDE RATIO, THROUGHPUT, TEMPERATURE, ADSORPTION, AND PROBABLE REACTION MECHANISM

The earlier work of Fischer and his co-workers showed that high pressure favored the formation of "Synthol" and of high-molecular-weight hydrocarbons and reduced the yield of liquid hydrocarbons per cubic meter of synthesis gas.[127] Pressures lower than atmospheric necessitated proportionately greater amounts of catalyst for equal conversion to hydrocarbons, although the average molecular weight and chemical composition of the product were unaffected by the reduced pressure.[128] This effect of pressures below 1 atmosphere is somewhat difficult to understand, as subsequent experiments with nickel-manganese-aluminum catalysts by Myddleton and Walker [129] showed that dilution of a mixture of equal parts of hydrogen and carbon monoxide with inert gases such as nitrogen increased the yield somewhat. It is possible that the slow step in the reaction is the desorption of the products, and that the rate of such desorption is directly proportional to the total gas pressure; this would be true if desorption due to molecular bombardment from the gas phase was very much more rapid than that due to energy transfer from the catalyst.

Tsuneoka and Fujimura [130] obtained data on the effect of diluents, particularly nitrogen, methane, and carbon dioxide, using a nickel-manganese-thoria catalyst. They found that gaseous mixtures containing less than 20 percent of these gases had no deleterious effect on the reaction. Lower yields, however, were obtained with 40 percent of nitrogen. Carbon dioxide was more effective than either nitrogen or methane in reducing the yield. With gradual dilution of the initial gas containing 2 parts of hy-

127 Fischer, F., and Küster, H., *Brennstoff-Chem.*, 14, 3–8 (1933).

128 Fischer, F., and Pichler, H., *ibid.*, 12, 365–72 (1931).

129 Myddleton, W. W., and Walker, J., *J. Soc. Chem. Ind.*, 55, 121-4T (1936).

130 Tsuneoka, S., and Fujimura, K., *J. Soc. Chem. Ind., Japan*, 37, Suppl. Binding, 704–11 (1934).

drogen and 1 of carbon monoxide, the molecular weight of the liquid hydrocarbon product decreased. The effect of carbon dioxide reported by Tsuneoka and Fujimura [130] should be compared with the results obtained by Fischer and Pichler [131] with various nickel, cobalt, and iron catalysts. They reported that whereas the presence of carbon monoxide in a carbon dioxide-hydrogen mixture retarded the catalytic hydrogenation, the presence of carbon dioxide in a carbon monoxide-hydrogen mixture exerted no influence on the yield of liquid hydrocarbons. No explanation of these conflicting reports concerning the effect of dilution with carbon dioxide is apparent.

The effect of increasing the carbon monoxide-hydrogen ratio is to produce more olefins and more carbon dioxide.[132]   A large excess of hydrogen produces a saturated product and favors methane formation. The percentage of olefins decreases in the order iron, cobalt, nickel (60, 40, and 5 percent, respectively, of olefins in the product) when these are used as catalysts, and increases with very short layers of catalyst (high space velocities). The yield of olefins is inversely proportional to the hydrogen content of the synthesis gas.[133]   A carbon monoxide-to-hydrogen ratio of 0.5 is the optimum for the maximum yield of hydrocarbons.[134]

A detailed study of the effect of pressures above atmospheric was made by

Fischer and Pichler [135] in 1939. As the pressure was increased above atmospheric, the yield at first increased and then (above 5 atmospheres) decreased. Table V shows the results with a cobalt-thoria-kieselguhr catalyst when 1 liter per hour of synthesis gas was used per gram of cobalt. The data are averages for 4 weeks' operation. Only a single pass of the gas through the catalyst was made, and no catalyst regenerating was done.

Martin [136] presented similar data on the effect of pressure on the total and fractional yields when employing two-stage operation. In Fischer and Pichler's data [135] the total yield of solid plus liquid hydrocarbons showed a minimum drop with time for reaction pressures of 5 to 15 atmospheres. At these pressures the initial yield was more than 150 grams per cubic meter and was still more than 100 grams per cubic meter after 26 weeks of operation. At atmospheric pressure the yield dropped from 130 to 100 grams per cubic meter in only 4 weeks of operation. At 150 atmospheres the drop in yield with time was very rapid. At such pressures there was a noticeable formation of cobalt carbonyl and consequent loss of activity of the catalyst; nickel catalysts deteriorated even more rapidly.

The slower drop in activity of the catalyst at medium pressures was shown also by the smaller temperature increase required to maintain maximum activity. Increasing time of operation was associated with a gradual drop in catalytic activity, presumably owing to the accumulation of solid hydrocarbons on the catalyst. This reduction could be partly compensated by raising the temperature at which the reac-

131 Fischer, F., and Pichler, H., *Brennstoff-Chem.*, **14**, 306–10 (1933).

132 Watanabe, S., Morikawa, K., and Igawa, S., *J. Chem. Soc., Japan,* **38**, Suppl. Binding, 328–31 (1935).

133 Murata, Y., and Tsuneoka, S., *ibid.,* **41**, Suppl. Binding, 16–22 (1938) ; *Sci. Papers Inst. Phys. Chem. Research (Tokyo),* **34**, 99–115 (1937).

134 Tsuneoka, S., and Fujimura, K., *J. Soc. Chem. Ind., Japan,* **37**, Suppl. Binding, 463–7 (1934).

135 Fischer, F., and Pichler, H., *Brennstoff-Chem.*, **20**, 41–61 (1939).

136 Martin, F., *Chem. Fabrik,* **12**, 238–8 (1939).

TABLE V

Effect of Pressures above Atmospheric on Yields of Products in Fischer-Tropsch
Synthesis [135]

Pressure atmospheres	Total Yield of Solid and Liquid Hydrocarbons	Paraffin Wax	Oil Boiling above 200° C	Gasoline Boiling below 200° C	Gaseous Hydrocarbons Including C_3 and C_4
		grams per cubic meter of synthesis gas			
1.0	117	10	38	69	38
2.5	131	15	43	73	50
6.0	150	60	51	39	33
16.0	145	70	36	39	33
51.0	138	54	37	47	21
151.0	104	27	34	43	31

tion was carried out. In the experiments at 5 to 15 atmospheres the initial temperatures of 175 to 180° C were not raised to 195° C even after 6 months' operation. At 1 atmosphere the initial 180° C had to be raised to 195° C after 5 weeks. The rate of temperature increase necessary to maintain activity was less if the paraffin was periodically removed from the catalyst by solvent extraction or by destructive distillation in a stream of hydrogen. The advantages of intermediate pressures for the hydrocarbon synthesis have been claimed in several patents.[137]

The effect of pressures up to 100 atmospheres on the synthesis of hydrocarbons on a ruthenium catalyst was studied by Fischer and Pichler [120] and by Pichler,[138] and up to 1,000 atmospheres by Pichler and Buffleb.[138] The results obtained in experiments at pressures from 15 to 1,000 atmospheres and at a temperature of 180° C are shown in Fig. 10. Three grams of ruthenium catalyst was used, and the flow of synthesis gas was so adjusted that 1 liter of effluent gas was obtained per hour. Under these conditions the conversion to hydrocarbons increased rapidly with increasing pressure up to about 300 atmospheres and more slowly above this pressure. At all pressures, solid paraffinic hydrocarbons constituted about 60 percent of the total yield of liquid plus solid hydrocarbons. The fraction of gaseous hydrocarbons in the products was approximately 25 percent for all pressures.

Operating at 10 atmospheres pressure with a cobalt-thoria-kieselguhr (100 : 18 : 100) catalyst and employing two-stage operation, Fischer and Pichler [139] studied the influence of contact time on the amount and nature of the hydrocarbons produced. The results are given in Tables VI and VII and are graphically presented in Fig. 11. Four grams of cobalt was contained in the second stage and 8 grams in the first stage. The apparatus consisted of two thermostated (with water-steam under pressure) 1-centimeter tubes with a trap for liquid hydrocarbons at the exit of each tube. For the first stage two tubes were connected in series, and contained in the same thermostat, and the depth of catalyst in each was about 50 centimeters. The temperature was adjusted in each test for optimum yield of liquid plus solid hydro-

137 Metallgesellschaft A.-G., Brit. Pats. 510,-850, 510,513–4 (1939).

138 Pichler, H., *Brennstoff-Chem.*, 19, 226–30 (1938). Pichler, H., and Buffleb, H., *ibid.*, 21, 257–64 (1940).

139 Fischer, F., and Pichler, H., *Brennstoff-Chem.*, 20, 221–8 (1939).
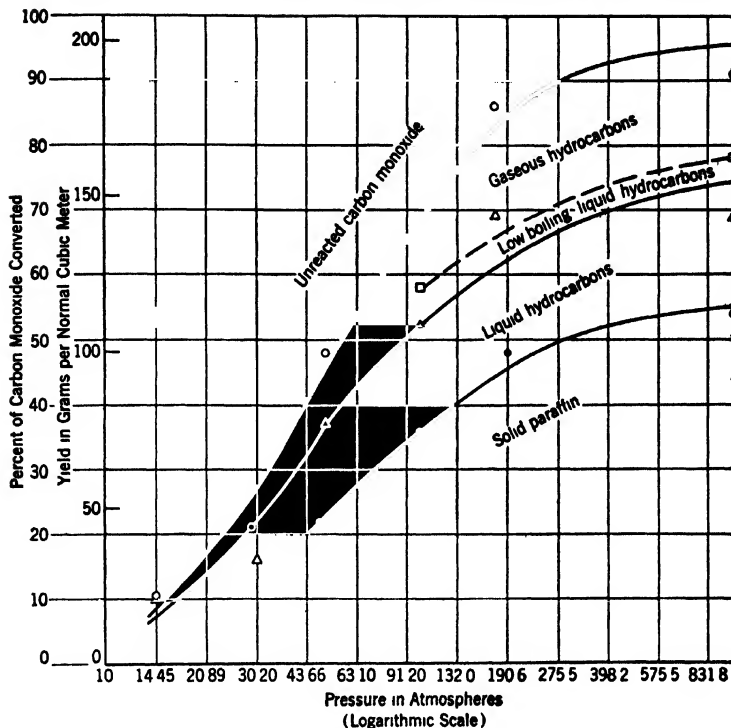
FIG 10   Yield and character of products from a ruthenium catalyst at 180° C.[188]

carbons   One of the outstanding facts shown by Table VI and Fig 11, in which the results of these tests are presented, is the extraordinarily small amounts of C_2 hydrocarbon produced   This marked discontinuity in the composition of the product should be correlated with Smith, Hawk, and Golden's [15] observations that ethylene, when added to the reactants, enters into the synthesis, although little or no reaction to form higher hydrocarbons occurs with ethylene alone or with ethylene plus either hydrogen or carbon monoxide alone   Craxford [140] confirmed the results obtained by

140 Craxford, S. R, *Trans Faraday Soc* **35**, 946–58 (1939)

these experimenters. This matter will receive further discussion in connection with speculations concerning the mechanism of the reaction.

The yield of solid paraffin decreased with increasing throughput, as did also the total yield of higher hydrocarbons.   Per cubic meter of synthesis gas, yields approaching 190 grams of solid, liquid, and gaseous ($C_3 + C_4$ only) hydrocarbons were obtained with a throughput of 0.2 liter per hour per gram of cobalt. This yield, consisting of 48 percent solid paraffin, 44 percent liquid hydrocarbons, and 8 percent of gasol ($C_3 + C_4$), formed about 90 percent of the theoretical (208 grams per cubic me-

TABLE VI

Intermediate Pressure Synthesis in Two Stages at Various Throughputs [139]

("Condensed" hydrocarbons are liquid at 10 atmospheres and room temperature)

Exp. No.	Time of Test days	Throughput, per Hour per Gram of Cobalt liters	Temperature First Stage °C	Temperature Second Stage °C	Contraction First Stage	Contraction Second Stage	Percent Conversion of Carbon Monoxide First Stage	Second Stage	Yield Condensed Hydrocarbons	Gasoline	C₃+C₄	C₂	C₁	Yield of C₃ and Higher Hydrocarbons Grams per Cubic Meter	Percent of Theoretical
					percent				grams per cubic meter						
1	22	1.12	189	189	56.5	81.5	62	89	141	15	10	2	16	166	80
2	23	1.11	190	190	55.5	81.1	60	88	140	15	10	2	17	165	80
3	23	1.15	192	192	59.0	82.0	64	89	134	..	..	..	..	...	..
4	24	0.87	190	192	60.0	84.4	65	92	144	15	12	2	19	171	82
5	26	0.87	189	192	55.0	84.4	61	92	142	15	12	2	21	169	81
6	28	0.43	190	192	69.5	84.5	78	98	133	.	..	..	..	...	..
7	29	0.83	191	192	65.8	84.1	74	94	144	16	13	1.4	19	173	83
8	30	0.46	186	187	69.0	85.3	78	96	148	..	..	..	..	...	..
9	31	0.48	184	185	....	85.2	..	95	150	14	15	2	13	179	86
10	33	0.43	184	184	66.0	85.1	72	94	151	14	15	2	12	180	86
11	34	0.43	185	185	64.0	84.7	72	95	150	14	15	2	12	179	86
12	35	0.27	178	177	69.0	86.1	75	96	157	11	16	1	12	184	88
13	36	0.24	175	177	....	85.1	..	94	158	11	16	1	7	185	89
14	37	0.25	177	177.5	69.0	86.1	76	98	159	11	16	1	11	186	89
15	40	1.02	195	195	48.5	75.0	54	82	114	24	20	2	12	158	76
16	41	1.09	198	198	51.0	77.1	57	84	114	24	20	2	14	158	76
17	42	2.13	212	212.5	61.0	77.0	70	88	98	26	19	1	35	143	69
18	43	2.16	213.5	214	59.0	76.5	66	87	96	26	19	1	33	141	68
19	44	1.3	202.5	202.5	59.0	79.7	65	88	118	24	20	2	20	162	78
20	45	1.26	204.5	204.5	60.0	79.4	68	90	115	24	20	2	21	159	76
21	47	1.28	205	205	62.0	79.8	69	90	116	24	20	2	23	160	77

TABLE VII

Estimates of Paraffin Yield [1]

Exp. No.	Throughput per Hour per Gram of Cobalt liters	Temperature °C	Paraffin Yield In Percent of Condensed Hydrocarbons First Stage	Second Stage	Grams per Cubic Meter of Synthesis Gas
13–14	0.24–0.27	175–178	52.8–54.6	54.5–56.0	86
4–5	0.87	189–192	40.4–40.7	40.2–40.8	58
15–16	1.02–1.09	195–198	33.0	31.4–32.9	37
17–18	2.13–2.16	212–214	20.4–20.8	19.2–21.6	20
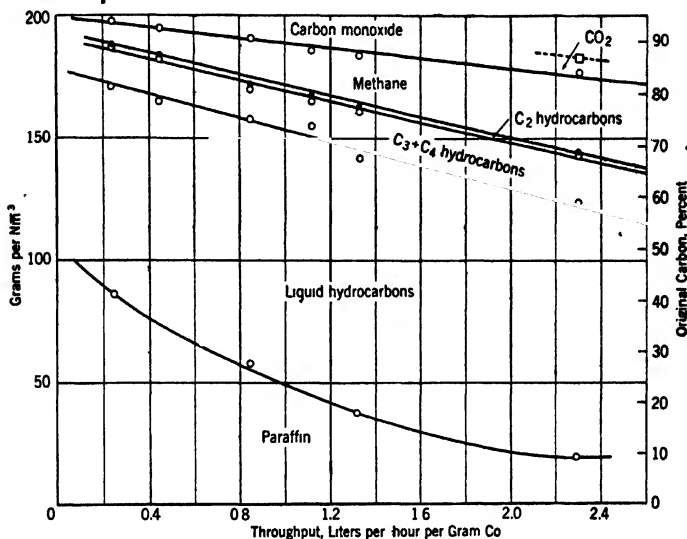
FIG. 11.   Intermediate pressure synthesis: cobalt catalyst, yields, and carbon balance versus throughput.[139]

ter). At a throughput of 2.0 liters per hour, 145 grams of hydrocarbons (excluding $C_1 + C_2$) were obtained, of which 14 percent was solid paraffin, 73 percent liquid hydrocarbons, and 13 percent gasol. The increased methane formation with increasing throughput, shown in Fig. 11, is due to the increasing optimum temperature (see Table VI). If the temperature is kept constant the yield of solid plus liquid hydrocarbons per cubic meter of synthesis gas drops rapidly with increased throughput. Table VIII contains some data obtained by Fischer and Pichler[135] at 200° C and 15 atmospheres with a cobalt-thoria-kieselguhr catalyst. Similar data were obtained by Tsuneoka and Fujimura[134] and by Aicher, Myddleton, and Walker.[141] Data obtained by Tsuneoka and Nishio[142]

141 Aicher, A., Myddleton, W. W., and Walker, J., J. Soc. Chem. Ind., **54**, 310-20T (1935).

142 Tsuneoka, S., and Nishio, A., J. Soc. Chem. Ind., Japan, **41**, Suppl. Binding, 11-6 (1938);

TABLE VIII

EFFECT ON YIELDS OF INCREASED THROUGHPUT AT CONSTANT TEMPERATURE [135]

Throughput, liters per hour per gram of cobalt	1.15	2.25	3.6	10.0
Yield, grams per cubic meter	101	85	60	16.5

at lower throughputs than given in Table VIII showed that the yield rose to a maximum with increasing throughput before decreasing.

The effect of increased throughput of synthesis gas with a ruthenium catalyst maintained at 230° C and under 100 atmospheres pressure is shown in Table IX.[143] The yield of solid plus liquid hydrocarbons (third, fourth, and fifth columns, Table IX) reaches a maximum at about 9 liters of gas per hour per gram of ruthenium.

Sci. Papers Inst. Phys. Chem. Research (Tokyo), **34**, 83-98 (1937).

143 Pichler, H., and Bußleb, H., Brennstoff-Chem., **21**, 273-80 (1940).

TABLE IX

EFFECT OF INCREASED THROUGHPUT WITH RUTHENIUM CATALYST AT 230° C [143]

Throughput, Liters per Hour per Gram of Ruthenium	Contraction Percent	Yield, Grams of Liquid per			Percent Conversion of Carbon Monoxide to Condensed Hydrocarbons	
		Cubic Meter of Gas	Gram of Ruthenium per Hour	Liter of Catalyst Space per Hour	Percent of CO Used	Percent of CO Reacted
1.8	81	136	0.24	108	78	87
3.2	79	125	0.40	180	72	83
4.3	69	98	0.43	194	56	74
7.0	62	84	0.59	265	48	70
9.1	56	79	0.72	324	45	..
10.7	50	65	0.69	310	37	68
16.7	36	37	0.60	270	21	54

The condensed hydrocarbons contained 65 to 68 percent of solid paraffinic hydrocarbons.

The temperature range over which the synthesis of hydrocarbons from hydrogen and carbon monoxide occurs is quite narrow. Even for the most active catalysts the reaction is very slow below 175° C, and above 225° C the rate of production of liquid hydrocarbon falls off sharply, and methane formation predominates.[144] The methane synthesis proceeds at a rapid rate at higher temperatures, such as 300 to 350° C. At such temperatures the main oxygenated compound formed is carbon dioxide rather than water, which is the chief oxygen-containing product at low temperatures.

Data given by Aicher and his coworkers [141] make it possible to calculate the temperature coefficient of the overall reaction on a nickel-manganese-aluminum catalyst at short contact times. For the temperature intervals 197 to 207° C and 191 to 270° C the coefficients per 10° C are 1.40 and 1.67. These coefficients are sufficiently larger than that of a diffusion process to suggest that the slow step is not the diffusion of reactants to, or of the products from, the catalyst surface through a "blanket" of high-boiling paraffin. Aicher and associates [141] plotted the yield of oil per unit time per volume of catalyst against the ratio of the concentration of the reactants to that of the products and obtained an almost straight line. This indicates that the reaction rate is directly proportional to the partial pressure of the reactants and inversely proportional to the concentration of the products. It is probable, therefore, that the slow step in the reaction is the desorption of the products from the catalyst surface.

Matsumura and his coworkers [145] studied the adsorption of hydrogen, carbon monoxide, carbon dioxide, and water on cobalt and iron catalysts which were active in the hydrocarbon synthesis. These adsorptions are of importance in any discussion of the reaction mechanism, and therefore the data concerning them are outlined briefly. The activated adsorption of hydrogen on the cobalt catalyst begins at 60° C and reaches a maximum at 160° C. On the iron

144 Tsuneoka, S., and Murata, Y., J. Soc. Chem. Ind., Japan, 37, Suppl. Binding, 711–6 (1934), 40, Suppl. Binding, 478–84 (1937).

145 Matsumura, S., Tarama, K., and Kodama, S., J. Soc. Chem. Ind., Japan, 43, Suppl. Binding, 175–84 (1940).

catalyst the corresponding temperatures are 60 and 190° C. Carbon monoxide is chemisorbed by the cobalt catalyst to form cobalt carbide at temperatures above 60° C, whereas the minimum temperature for carbide formation on the iron catalyst is 190° C. The activated adsorption of water on the cobalt catalyst begins at 30° C and reaches a maximum at 100° C, and at about 200° C (optimum temperature for hydrocarbon synthesis) very little adsorption occurs. On the iron catalyst, activated adsorption of water begins at 200° and increases slowly with increasing temperature. The activated adsorption of carbon dioxide on the cobalt catalyst begins at 100° C and reaches a maximum at 150° C and then decreases slowly with rising temperature. On the iron catalyst there is evidence for activated adsorption of carbon dioxide to only a slight extent at 200 to 250° C.

Craxford[140] and Craxford and Rideal,[146] in a study of the kinetics of the hydrocarbon synthesis, obtained results that may be summarized as follows: (1) At the temperature of the synthesis carbon monoxide reacts slowly with a cobalt catalyst to give cobalt carbide, according to the equation: $2Co + 2CO = Co_2C + CO_2$; but this reaction is always slower than the reduction of the carbide by hydrogen at the same temperature. (2) At this temperature the catalyst reacts with carbon monoxide and hydrogen to give carbide, that is, $2Co + CO + H_2 \rightarrow Co_2C + H_2O$; and this reaction is faster than the reduction of the carbide by hydrogen under the synthesis conditions. (3) Reduction of cobalt carbide may lead to methane or to higher hydrocarbons, according to the conditions, and the experiments showed that, when normally liquid hydrocarbons are being

produced, the ortho-para-hydrogen conversion is inhibited, indicating that very little chemisorbed hydrogen occurs on the catalyst surface. (4) Whenever methane is the main product of the hydrocarbon synthesis, the ortho-para-hydrogen conversion occurs freely, showing that chemisorbed hydrogen is then present. (5) The water-gas shift reaction, i.e., $CO + H_2O = CO_2 + H_2$, runs parallel to the ortho-para-hydrogen conversion; it occurs when methane is being formed but is inhibited when normally liquid hydrocarbons are being produced. (6) The hydrogenation cracking of paraffin hydrocarbons on catalysts active for hydrocarbon synthesis is similarly inhibited when liquid hydrocarbons are being produced and also by the presence of carbide on the catalyst surface, but otherwise it occurs freely at similar temperatures. (7) Craxford[140] verified Smith and his coworkers'[15] results concerning the effect of ethylene on the synthesis, which gives an increased yield of liquid hydrocarbons and appreciable amounts of oxygenated organic compounds.

Before discussing the probable mechanism of the reaction, mention should be made of the fact, disclosed by several experimenters,[18, 126] that during the first few hours after a freshly reduced catalyst is exposed to synthesis gas only methane and carbon dioxide are produced. Some of the more active cobalt catalysts will produce methane and water (instead of carbon dioxide) during this initial period. It may be necessary to use the following procedure[126] to start the synthesis. The temperature should be well over 150° C when synthesis gas is first admitted to replace hydrogen. The temperature should then be raised very slowly, a satisfactory procedure being to hold the temperature constant for 2 hours when the contraction reaches 20 percent, then again constant for 2 hours

146 Craxford, S. R., and Rideal, E. K., *J. Chem. Soc.*, **1939**, 1604–14.

at 30 percent, 40 percent, and so on. In this way it has been possible to induce oil formation in a minimum of time on any sample of active catalyst.

It is agreed by most investigators that the first step in the synthesis of hydrocarbons from hydrogen and carbon monoxide is, that proposed by Fischer and his co-workers,[2, 3] namely, the formation of metal carbides, as, for example: $3Co + CO = Co_2C + CoO$. Craxford[140] wrote the primary reaction as $2Co + CO + H_2 = Co_2C + H_2O$. Matsumura,[145] however, preferred to postulate the transient existence of the metal oxide. Subsequent reduction with hydrogen to form chemisorbed water would account for the elimination of the oxygen as water on cobalt catalysts. However, on iron catalysts the chemisorption of water at 200° C is much larger than for cobalt at the same temperature, and hence there is more opportunity for carbon monoxide to form carbon dioxide by reaction with the oxygenated areas on the catalyst surface; and this accounts for the fact that for iron catalysts the oxygen appears in the reaction products largely as carbon dioxide.

The second step in the synthesis is the reduction of the carbide to a methylene group. Craxford[140] postulated that this reaction is with molecular hydrogen $Co_2C + H_2 = CH_2 + Co$, because his work on the ortho-para-hydrogen conversion on hydrocarbon synthesis catalysts showed that whenever atomic hydrogen was present only methane, and not higher hydrocarbons, was produced. Matsumura[145] pointed out that this coincidence does not necessarily mean that methylene cannot be formed by reaction of the carbide with atomic hydrogen produced by activated adsorption on the catalyst surface. Indeed, such participation of active hydrogen is very probable, as the temperature range

for active higher-hydrocarbon synthesis, 175 to 200° C, coincides with that for the maximum amount of activated adsorption of hydrogen. The somewhat higher optimum temperature for iron as compared with cobalt catalysts was explained by Matsumura[145] as being due to the higher temperature necessary for maximum chemisorption of carbon monoxide on iron. The ortho-para-hydrogen conversion does not proceed to any appreciable extent during active synthesis of higher hydrocarbons because most of the active catalyst surface is covered with methylene or polymethylene groups.

The extent of the polymerization of the methylene groups is determined by the rate of desorption of the $(CH_2)_n$. Therefore, on the catalyst surface a "steady state" is set up which involves polymerization, reduction, and desorption of the methylene and polymethylene groups. If the extent of carbide formation is small, or if the rate of desorption of the methylene group is rapid, the concentration of methylene groups on the catalyst surface is low, polymerization is therefore retarded, methane is the main product, and there is an ample supply of active surface on which the ortho-para-hydrogen reaction may proceed. The absence of higher-hydrocarbon formation during the initial period of operation with an active catalyst is to be explained by the time necessary for covering most of the catalyst surface with polymethylene groups so as to slow up the reduction of methylene to methane. Predominant methane formation at higher temperatures, above 250° C, is due to the very rapid desorption of methylene groups.

When carbon monoxide is adsorbed in the outer adsorption layers and not in direct contact with the catalyst surface its reduction leads to compounds containing oxygen rather than hydrocarbons. These

are the conditions that exist when an appreciable concentration of ethylene is provided in the synthesis gas, and when pressures of 100 to 200 atmospheres are employed.

PROPERTIES OF FISCHER-TROPSCH SYNTHESIS PRODUCTS: GASOLINE, DIESEL FUEL, PARAFFIN WAX, LUBRICATING OIL, AND FATTY ACIDS

The primary product of the Fischer-Tropsch synthesis, labeled "Kogasin" by Fischer, has been shown [147] to contain largely straight-chain paraffinic and olefinic hydrocarbons with only very minor amounts of aromatic hydrocarbons, naphthenes, and oxygenated organic compounds.

Table X contains data on the boiling ranges and olefin contents of various fractions of the primary product obtained in Fischer's [147] laboratory from a cobalt catalyst. Gasoline boiling to 200° C constituted 60 percent of the total product. The gasoline fraction boiling to 150° C was collected by adsorption on active charcoal. Its density was 0.680 at 20° C, and, despite an olefin content of 45 percent, the octane rating was only about 55. Fischer [147] claimed that this rating might be increased to 72 by the addition of 0.5 cubic centimeter of tetraethyl lead per liter of gasoline. The only refining necessary was a wash with alkali to remove traces of fatty acids.

The data of Table X are in accord with the statement by Martin [25] that the average olefin content of the product obtained in the plants in operation up to August,

[147] Tsuneoka, S., and Fujimura, K., *J. Soc. Chem. Ind., Japan*, **37**, Suppl. Binding, 49–51 (1934). Tsuneoka, S., and Murata, Y., *ibid.*, **38**, Suppl. Binding, 212–7 (1935). Firsanova, E. N., *Khim Tverdogo Topliva*, **8**, 892–901 (1937). Fischer, F., *Ber.*, **71A**, 56–67 (1938). *Dept. Sci. Ind. Research (Brit.), Fuel Research Board, Rept. for the Year Ended March 1938*, pp. 195–7.

TABLE X

COMPOSITION OF KOGASIN [147]

Constituents	Percent by Weight	Olefin Content volume percent
Gasol (C₃ + C₄)	8	55
Gasoline to 150° C	46	45
Gasoline 150 to 200° C	14	25
Diesel oil	22	10
Paraffin wax from oil (melting point 50° C)	7	..
Paraffin wax from catalyst (melting point 90° C)	3	..

1937, that used cobalt catalysts throughout was 29 percent, the majority of the olefins being in the fraction boiling below 200° C. If the product boiling above 200° C was cracked, by means of techniques well known to the petroleum industry, and the cracked gasoline was mixed with the primary Kogasin boiling to 200° C, there was obtained, in about 80 percent yield, the finished gasoline with approximately 195° C distillation end point, 68 octane number, and 0.728 density at 15° C.

Snodgrass and Perrin [148] have reported data obtained by the Ruhrchemie A.-G. in Germany on a two-stage operation, the first stage being at atmospheric pressure and the second at several atmospheres. These data are given in Tables XI and XII. Though very little paraffin wax was produced in the first stage, the second stage alone yielded twice as much of this product as was reported by Fischer. [147] The second stage yielded 43 percent of oil boiling above 300° C, whereas only 15 percent of the first-stage oil boiled above that temperature. The olefin content of the second-stage gasoline from the charcoal scrubbers was lower than that of the first stage. The octane rating of the 30 to 140° C gasoline was 62; that of the 30 to 110° C was 67.

[148] Snodgrass, C. S., and Perrin, M., *J. Inst. Petroleum Tech.*, **24**, 289–301 (1938).

TABLE XI

PROPERTIES OF PRODUCTS FROM TWO-STAGE OPERATION [148]

Constituent	Boiling Range °C	Specific Gravity	Olefins First Stage	Olefins Second Stage	Percent by Weight of Total Product First Stage	Percent by Weight of Total Product Second Stage
			volume	percent		
Gasol ($C_3 + C_4$)	....	....	50	25–30	5	2
Gasoline to 150° C	30–150	0.66	35–40	20	26.5	8
Oil over 150° C	100–300	0.74	12	12	26.5	11
Paraffin wax	....	0.85	....	....	....	21

TABLE XII

DISTILLATION OF KOGASIN FROM TWO-STAGE OPERATION [148]

Temperature °C	Percent by Volume First Stage	Percent by Volume Second Stage
30	0.0	0.0
50	8	3
100	29	14
150	47	24
200	60	35
250	75	48
300	85	57

The operation of a vapor-phase cracking process for the higher-boiling oils was also described by Snodgrass and Perrin.[148] The octane rating of the products was 62 to 75.

The desirability of operating the Fischer-Tropsch synthesis in two or more stages has been generally recognized. Production in the two-stage process is increased by about 20 percent over the single-stage operation, and the life of the catalyst is increased considerably.[125, 149] The so-called Robinson-Bindley process not only was operated in several stages but has also been reported to have developed a sulfur-resist-ant catalyst that is active in the synthesis of monoolefins but only slightly active for hydrogenation.[150] The principal constituent of the catalyst used was cobalt, to which a small amount of potassium carbonate was added. Blue water gas ($H_2 : CO = 1$) containing appreciable quantities of sulfur was the synthesis gas used with this catalyst. Myddleton[125] stated that the fraction boiling up to 150° C of the primary product of the Robinson-Bindley or Synthetic Oils procedure contained 70 percent of olefins and had an octane rating (motor) of 68, which could be raised to 80 by adding 4 cubic centimeters of tetraethyllead per liter.

Diesel oil can be isolated from Kogasin by simple distillation. The Diesel oil obtained has a boiling range of about 200 to 360° C, a specific gravity (at 20° C) of 0.769, a hydrogen content of 15.2 percent, a heat of combustion of 10,470 to 11,300 calories per gram (18,900 to 20,300 Btu per pound), and a cetene value of over 100. This material, because of its high heat of combustion and high cetene number, is particularly suitable for mixing with and improving oils of lower ignitibility, such as tar oils[151] and especially heavy petroleum oils. Generally, an addition of 30 to 40 percent of Fischer-Tropsch Diesel oil suffices. The increased olefin production in the Synthetic Oils process, which results in a higher octane rating for the gasoline produced, also causes the Diesel oil fraction to have a lower cetene number, but the quality is still high; Myddleton[125] reported 81 and 86 for the 200 to 300° C and 200 to 290° C fractions, respectively. Hydrogen-

[149] Fischer, F., and Pichler, H., *Brennstoff-Chem.*, **17**, 24–29 (1936). Studien-und-Verwertungs G.m.b.H., Brit. Pat. 454,948 (1936). Synthetic Oils Ltd. and Myddleton, W. W., Brit. Pat. 491,778 (1938).

[150] Anon., Colliery Guardian, **159**, 203 (1939); *Chem. Trade J.*, **104**, 200 (1939). Myddleton, W. W., Brit. Pat. 509,325 (1939).

[151] Uhde, F., and Pfirrmann, T. W., Brit. Pat. 482,783 (1938). Kolbel, H., *Brennstoff-Chem.*, **20**, 352–5, 365–9 (1939). Anon., *Nat. Petroleum News*, **31**, No. 28R, 296 (1939).

ation, of course, will increase the cetene number.[149]

Paraffin wax with melting points ranging from 50 to 100° C and with molecular weights up to 2,000 are produced by the hydrocarbon synthesis on cobalt, nickel, or iron catalysts.[148, 152] In a study of the behavior of ruthenium, osmium, platinum, iridium, and palladium as catalysts, Pichler[138] showed that ruthenium is far more effective than iron, cobalt, or nickel in producing solid hydrocarbons. By a single pass of synthesis gas at 1 liter per gram of ruthenium per hour over the catalyst at 195° C and 100 atmospheres pressures, 100 grams of solid paraffin and 50 grams of oil were obtained per cubic meter of gas. A 6 months' test showed no appreciable change in catalyst activity. The solid paraffin was snow white in the crude state and melted to a clear liquid at 118 to 119° C. By solvent extraction it was possible to isolate from the crude paraffin hitherto unknown solid paraffin hydrocarbons with melting points up to 132° C and molecular weights of 7,000 to 9,000. Additional information on the properties of the solid products obtained by the use of a ruthenium catalyst has been presented by Pichler and Buffleb,[153] who separated the solid paraffins by extraction with various solvents. The physical properties of the fractions are shown in Table XIII; the highest melting point was in the range 132 to 134° C corresponding to an average molecular weight of 23,000.

For motor-fuel purposes it is essential in a Fischer-Tropsch plant to provide for the cracking of high-boiling products so as to produce a large amount of higher-octane gasoline. Investigations in Fischer's laboratory[154] and by Egloff and his associates[154] showed that yields of about 75 to 80 percent by weight of a cracked gasoline may be obtained, which, when mixed with 42 to 30 percent of the primary gasoline fraction of the synthesis product, had an octane rating of 63 to 70. Davies[155] has described a cracking plant designed by True Vapor Phase, Ltd., and erected alongside the Fischer-Tropsch plant at Oberhausen-Holten in Germany. Snodgrass and Perrin[148] presented some data that were obtained with primary Fischer-Tropsch product in a True Vapor Phase control unit. These results, which are reproduced in Table XIV, were stated to have been confirmed in commercial operation. In a patent[156] concerned with cracking Fischer-Tropsch primary synthesis product it was stated that, if this product was first acid-washed and treated with "bleaching earth," the amounts of gas and coke produced were greatly reduced.

The primary product of the Fischer-Tropsch synthesis does not contain any lubricating-oil fractions but it does contain large amounts of olefins, which can be readily polymerized to yield good lubricating oil. Several possible procedures for the production of lubricating oil from the hydrocarbon synthesis products have been tested, namely, (1) chlorination of the gas-oil fraction (boiling point > 200° C) and mixing the products with aromatic hydrocarbons in the presence of aluminum chloride; (2) chlorination of the gas-oil frac-

[152] Koch, H., and Ibing, G., *Brennstoff-Chem.*, **16**, 141–5 (1935). Graefe, E., *J. Inst. Petroleum Tech.*, **23**, 78A (1936). Studien-und-Verwertungs G.m.b.H., Brit. Pats. 500,950, 517,002 (1939).

[153] Pichler, H., and Buffleb, H., *Brennstoff-Chem.*, **21**, 285–8 (1940).

[154] Pichler, H., *Brennstoff-Chem.*, **16**, 404–6 (1935). Peters, K., and Winzer, K., *ibid.*, **17**, 301 6 (1936). Egloff, G., *ibid.*, **18**, 115–7 (1937). Egloff, G., Nelson, E. F., and Morrell, J. C., *Ind. Eng. Chem.*, **29**, 555–9 (1937).

[155] Davies, V., *Ind. Chemist*, **13**, 442–6 (1937).

[156] I. G. Farbenindustrie A.-G., Brit. Pat. 480,442 (1938).

TABLE XIII

SOLVENT EXTRACTION OF SOLID PARAFFIN OBTAINED BY USE OF A RUTHENIUM CATALYST AT
1,000 ATMOSPHERES PRESSURE [153]

Fraction No.	Solvent	Extraction Temperature °C	Percent Dissolved	Melting Point °C	Density 20° C	Density 150° C	Average Mol. Wt.	Viscosity 150° C	Viscosity 180° C
								centistokes	
1	n-Pentane	34	30–33	51–57	.....	.....	......	......	......
2	n-Hexane	68	14–17	92.5–95	.....	0.765	760	6	4
3	Kogasin fraction	90	14–16	121–122.5	0.966	0.778	1,750	29	17
4	n-Heptane	98	20–25	129.5–130.4	0.978	0.783	6,750	870	410
5	Kogasin fraction	121	12–15	132–134	0.980	0.786	23,000	35,600	15,800

tion and polymerization without addition of aromatic hydrocarbons; (3) direct catalytic polymerization of the olefins produced in the synthesis; and (4) chlorination of the paraffin wax, followed by elimination of hydrochloric acid and polymerization of the resulting olefins. Of these procedures, the third has received most attention.[157] Pichler's results [157] showed that

157 Fischer, F., Koch, H., and Wiedeking, K., *Brennstoff-Chem.*, 15, 229–33 (1934). Koch, H., and Ibing, G., *ibid.*, 16, 185–90 (1935). Pichler, H., *Z. Ver. deut. Ing.*, 79, 883–5 (1935), 80, 49–51 (1936). I. G. Farbenindustrie A.-G., Fr. Pat. 802,208 (1936). Brit. Pat. 494,657 (1938). Studien-und-Verwertungs G.m.b.H., Brit. Pat. 453,973 (1936). Koch, H., *Brennstoff-Chem.*,

oils prepared from the olefins in Kogasin by the action of anhydrous aluminum chloride had flat viscosity-temperature curves (viscosity index 90 to 100); and for the same viscosity they had a higher mean molecular weight than paraffin-base mineral lubricating oils. The viscosities of the fractions and residue obtained on distillation of the oil *in vacuo* increased regularly with the molecular weight. The olefinic bonds in the lubricating oils were readily hydrogenated, for example, by the

18, 121-7 (1937). Ruhrchemie A.-G., Fr. Pat. 809,226 (1937); Brit. Pats. 470,534, 473,935 (1937), 490,930 (1938), 503,206, 504,350 (1939).

TABLE XIV

PROPERTIES OF GASOLINE OBTAINED BY CRACKING OF KOGASIN
IN TRUE VAPOR PHASE OPERATION [148]

Charge	Reduced Crude Specific Gravity 0.769			Untopped Crude Specific Gravity 0.725	
Cracked gasoline:					
Yield, weight percent	81	75.5	65.2	70.6	65.2
Yield, volume percent	88	81.8	73	72	68.3
Specific gravity	0.7079	0.7906	0.6876	0.7114	0.6920
End point, °C	200	197	168	197	160
Octane No. (motor)	62	68	75	67	73
Lead tetraethyl to raise octane number to 80, cubic centimeters per Imperial gallon	......	3.5	1.3	3.7	1.7

action of hydrogen at 180° C, and at 100 atmospheres, in the presence of a nickel catalyst.

The lubricating oils were as stable towards air and light as mineral lubricating oils; their stability was increased by hydrogenation. Subjected to the British Air Ministry oxidation test, the oils showed a greater increase in viscosity but a smaller increase in Conradson carbon than mineral lubricating oils. Similar results were obtained in tests on lubricating oils produced by polymerization of the 80 to 140° C Kogasin fraction made in the British Fuel Research Board Laboratory [158] and of the 150 to 200° C fraction of the product obtained by Synthetic Oils, Ltd.[125] Aging by the Indiana oxidation test [159] showed that, as compared with natural products, a sample of the synthetic lubricating oil gave upon oxidation a large increase of viscosity that was associated with the formation of acidic and saponifiable substances, although the amounts of asphalt or coke formed were extremely small. According to Fischer,[147] very thorough hydrogenation of the synthetic oils increased the chemical stability so that no attack by oxygen or concentrated sulfuric acid could be detected, and no corrosion of motor metal parts was observable in a 6 months' road test.

According to the Ruhrchemie A.-G. patents,[157] it is advantageous, in the synthesis of lubricating oil from Kogasin, to use enough of the polymerizing agent (usually aluminum chloride) to effect complete reaction at a single temperature and to raise the temperature gradually during the process. The polymerizing agent may be used more than once. The properties of the lubricating oil obtained depend to a large extent on the boiling range and olefin content of the Kogasin fraction used. Koch's results [160] showed that the higher-boiling Kogasin fractions yielded lubricating oils of highest viscosity index. Unfortunately, the yield was small because of the low olefin content of the high-boiling Kogasin fractions.

Koch [160] also found that the synthetic lubricating oil contained one or two double bonds per molecule, and solvent extraction with acetone showed that the degree of unsaturation was about the same for all the fractions thus obtained. Analysis of the oil by Waterman's method showed the presence of about one naphthenic ring per molecule. Since this was true for all the fractions selectively extracted by acetone, pure isoparaffins were present in only small proportions. Kreulen [161] determined the chemical and physical constants of two completely hydrogenated lubricating oils obtained by polymerization of Kogasin fractions and subsequent hydrogenation. He found that about 50 percent of the carbon atoms in the synthetic oils occurred in branched paraffin chains. This is in marked contrast to Koch's [160] results with the same type of oils before hydrogenation. The hydrogenated oils, upon analysis by the Waterman method, showed 1.2 to 1.8 rings per molecule, but from parachor measurements the number of rings was 2.3 to 4.0.

Koch and Gilfert [162] studied the properties of oils produced by polymerization of Kogasin fractions produced from $CO : H_2$ and from $CO : 2H_2$. Fractions from the $CO : H_2$ Kogasin corresponding to C_5, C_6, and C_7 hydrocarbons and containing 70 to

[158] *Dept. Sci. Ind. Research (Brit.), Fuel Research Board, Rept. for Year Ended March, 1938*, p. 201.

[159] Kadmer, E. H., *Chem.-Ztg.*, **62**, 611–3 (1938).

[160] Koch, H., *Brennstoff-Chem.*, **19**, 337–43 (1938).

[161] Kreulen, D. J. W., *Chem. Weekblad*, **36**, 410–1 (1938).

[162] Koch, H., and Gilfert, W., *Brennstoff-Chem.*, **20**, 413–20 (1939), **21**, 1–7 (1940).

75 percent of olefins gave about 65 percent (calculated on the olefin content) of lubricating oil of 1,110 to 1,550 centistokes viscosity at 20° C and viscosity pole height of 1.88 to 2.33. The corresponding fractions from $CO : 2H_2$ Kogasin contained 43 to 55 percent olefins and yielded only 35 to 55 percent of oils of viscosity 473 to 585 centistokes at 20° C and viscosity pole heights of 2.23 to 3.10; this lubricating oil was obviously much inferior to that from the $CO : H_2$ Kogasin. The lower yields from the $CO : 2H_2$ Kogasin were not due to the lower olefin content of the raw material but to a difference in constitution of the olefins. The C_6 and C_7 fractions of the $CO : H_2$ Kogasin were refractionated into narrow cuts, from each of which a lubricating oil was synthesized. The viscosity of the oils from the C_6 fractions ranged from 2,277 (from 57.0 to 61.0° C fraction) to 476 (from 67.5 to 69.0° C fraction) centistokes at 20° C. The flattest viscosity-temperature curve (corresponding to a viscosity pole height of 1.77) was given by the oil from the 63.0 to 63.5° C fraction, which was principally hexene-1. The steepest curve, corresponding to a viscosity pole height of 2.53, was obtained from the 67.5 to 69.0° C fraction, which was principally hexene-2. The C_7 fractions showed similar but somewhat less marked differences. There was no apparent relation between the absolute viscosities of the oils and the viscosity pole height. The mean molecular weight of the lubricating oils ranged from 550 to 1,240.

By reducing the temperature of polymerization of a C_5 Kogasin fraction from 20 to 0° C, Koch and Gilfert [162] obtained a more viscous lubricating oil of the same viscosity index. All the lubricating oils produced had one olefinic bond. Saturation of this bond with hydrogen resulted in a small increase in viscosity but no change in viscosity index. Examination by Waterman's method indicated the presence of one naphthenic ring per molecule.

Imperial Chemical Industries, Ltd., has several patents covering the synthesis of lubricating oil from Kogasin by chlorination of the high-boiling fraction and of paraffin wax followed by condensation with aromatic hydrocarbons using aluminum chloride as catalyst.[163] The I. G. Farbenindustrie A.-G. has patented a process for lubricating-oil production, in which a Kogasin fraction boiling between 170 and 250° C is subjected to high-frequency silent electric discharge at, for example, 7,000 volts and 1,000 cycles for 20 hours at a pressure of 2 to 5 millimeters of mercury.[164]

The fatty acids formed in small quantities during the synthesis of Kogasin amount to about 0.35 percent by weight, referred to the main liquid hydrocarbon product. By fractionation, formic, acetic, propionic, and butyric acids were detected.[165] Two-thirds of the mixed water-soluble fatty acids consisted of acetic acid. No unsaturated acids were found. The fatty acids dissolved in the Kogasin amounted to about 0.06 percent and consisted of acids of 5 to 10 carbon atoms per molecule, but acids of still larger molecular weight were detected in smaller quantities.

Since 1936 there has been a rapid development, particularly in Germany, of the art of production of fatty acids by the oxidation of the paraffin wax produced in the Fischer-Tropsch synthesis.[166] In 1938

[163] Lowes, A. P., White, E. W., and Imperial Chemical Industries, Ltd., Brit. Pats. 483,316, 485,165 (1938). Lowes, A. P., and Imperial Chemical Industries, Ltd., Brit. Pat. 493,715 (1938).

[164] I. G. Farbenindustrie A.-G., Brit. Pat. 485,-478 (1938).

[165] Koch, H., Pichler, H., and Kolbel, H., Brennstoff-Chem., **16**, 382–7 (1935).

[166] Imhausen, A., Fette u. Seifen, **44**, 411–5 (1937); Kolloid-Z., **85**, 284–46 (1938). Henk,

two plants each of 20,000 tons per year were reported.[167] Paraffins can be oxidized by air. The reaction is strongly exothermic, but, when carefully controlled, mainly monocarboxylic acids are produced along with minor amounts of alcohols. The addition of partly oxidized paraffins to the raw material accelerates the reaction. Paraffins with over 34 carbons are most suitable for the process. Operating conditions are 140 to 160° C, 1 cubic meter of air per kilogram of wax, and the presence of catalysts such as manganese [168, 169] and other metal [170] salts of fatty acids. The crude saponification product is purified by treatment with steam [169] and by solvent extraction.[170]

Jantzen and his coworkers [171] studied the composition of the fatty acids obtained from the oxidation of Fischer-Tropsch paraffin wax containing 27.4 percent of C_{16}-C_{19}, 31 percent of C_{19}-C_{22}, 23.7 percent of C_{22}-C_{25}, 11.7 percent of C_{25}-C_{27}, and 1.7 percent C_{28} hydrocarbons. The oxidation product consisted almost entirely of saturated, normal, fatty acids of both the odd and even series, among which the acids from C_8 to C_{18} were separated and identified by fractionation of the methyl esters. Acids with less than 8 and more than 18 carbon atoms per molecule formed 7.4 and 18 percent, respectively, of the total product. The balance consisted of approximately equimolecular proportions of C_9 to C_{15} acids. Small amounts of unsaturated and of hydroxy acids were present.

The oxidation of Fischer-Tropsch olefins containing more than 6 carbon atoms using hydrogen peroxide yields soap-forming carboxylic acids.[172]

ECONOMICS OF COAL AND CARBON MONOXIDE HYDROGENATION

Schultes,[173] in a very informative paper on the production of water gas and of synthesis gas, has presented comparative cost data on various processes for the production of synthesis gas $(2H_2 + CO)$. The cheapest process was reported to consist of complete gasification of bituminous coal in a Bubiag-Didier generator, the cost per cubic meter being 0.0107 Reichsmark (RM), and the cost of synthesis gas necessary to produce 100 kilograms of oil being 10.4 RM. At 40 cents per RM, these figures are 12 cents per 1,000 cubic feet of synthesis gas and $37.70 per ton (2,000 pounds) of oil. Schultes derived his costs on the basis of 11.25 RM ($4.50) per ton of slack coal, 0.02 RM (0.8 cent) per kilowatt-hour, 0.06 RM (2.4 cents) per cubic meter of cooling water, and 3 percent and 12.5 percent of total capital costs for main-

H. J., *Seifensieder-Ztg.*, **64**, 1001–2 (1937). Wietzel, G., *Angew. Chem.*, **51**, 531–7 (1938); *Chem. Age*, **39**, 278–80 (1938); *Klepzig's Textil-Z.*, **41**, 528–9 (1938); *Fette u. Seifen*, **46**, 21 5 (1939). Meyer, W., *Seifensieder-Ztg.*, **65**, 215–7, 238–9, 256–7, 277–8, 297–9, 317 9, 338–40 (1938); *Süddeut. Apoth.-Ztg.*, **78**, 47–9 (1938). Selasinsky, A., *Rundschau deut. Tech.*, **18**, 9 (1938). Bauschinger, C., *Fette u. Seifen*, **45**, 629 (1938). Henblum, R., *Riv. ital. essenze profumi e piante offic.*, **20**, 236 7, 304 5 (1938). Schrauth, W., *Chem.-Ztg.*, **63**, 274 8 (1939). Lemaire, E, *Génie civil*, **115**, 413–7 (1939). Wolff, B., *Przemysl Chem.*, **23**, 51 -4 (1939).

167 Anon., *Brennstoff Chem*, **19**, W8 (1938); *Ind. Eng. Chem., News Ed.*, **16**, 193 4 (1938). Wittka, F., *Seifensieder-Ztg*, **66**, 666–8 (1939). Foulon, A., *Mfg. Perfumer*, **4**, 150–1 (1939).

168 *Dept. Sci. Ind. Research (Brit.), Fuel Research Board, Rept. for the Year Ended March 1938*, pp. 205–6. I. G. Farbenindustrie A. G., Brit. Pat. 490,785 (1938).

169 I. G. Farbenindustrie A.-G., Brit. Pats. 482,277, 487,317 (1938). Farenholtz, W. A., Hubbe, G., and Hubbe, H., Brit. Pat. 506,104 (1939).

170 Henkel & Co. G.m.b.H., Brit. Pat. 489,443 (1938). Farenholtz, W. A., Hubbe, G., and Hubbe, H., Brit. Pat. 507,521 (1939).

171 Jantzen, E., Rheinheimer. W., and Asche, W., *Fette u. Seifen*, **45**, 388–93, 613–5 (1938).

172 Deutsche Hydrierwerke A.-G., Brit. Pat. 492,595 (1938).

173 Schultes, W., *Glückauf*, **72**, 273–85 (1936).

tenance and amortization plus interest, respectively. Steam costs were not given and apparently were overlooked; at 40 cents per 1,000 pounds of steam the costs should be increased by about 10 percent to provide the necessary amount of steam. Schultes' costs also included 6 percent of the capital investment for a combination of miscellaneous charges including sulfur removal. The capital investment for a plant producing 665,000 cubic meters (23,500,000 cubic feet) of gas per day (amount of gas necessary to produce 25,000 metric tons per year of oil) was estimated to be 5,365,-000 RM, or $2,146,000. The gas produced was assumed to contain about 14 percent of carbon dioxide.

The cost of producing water gas from coke by means of the standard air and steam blasts was given by Schultes as about 0.019 RM per cubic meter; coke was charged at 21.5 RM per metric ton. This cost per cubic meter of gas was about 90 percent higher than that given for the Didier generator; the chief item responsible for the increase was the higher cost of coke as compared with coal. However, the cost of enough water gas from coke to produce 100 kilograms of oil was 16.5 RM, or only about 60 percent more than that for gas from the Didier process, owing to the higher yield of synthesis gas from the water gas produced from coke.

Laupichler [174] has presented some cost data on the production of hydrogen by the catalytic water-gas shift reaction, $CO + H_2O \rightarrow CO_2 + H_2$. He indicated a cost of about 15 RM per 1,000 cubic meters (17 cents per 1,000 cubic feet) of ammonia synthesis gas produced by the water-gas shift reaction, beginning with a mixture of water gas and producer gas containing 39 percent carbon monoxide, 33 percent hydrogen, 7 percent carbon dioxide, and 21 percent nitrogen. If the producer gas were omitted, so as to produce hydrogen instead of ammonia synthesis gas, the production cost should be about 10 percent greater. Laupichler's costs were based on 0.025 RM (1.0 cent) per kilowatt-hour for power and 3.5 RM per 1,000 kilograms (64 cents per 1,000 pounds) for steam. Laupichler's total cost for removal of carbon dioxide from the shifted gas was 9 RM per 1,000 cubic meters, whereas that given by Schultes [173] was only 2 RM per 1,000 cubic meters. Part of this discrepancy apparently is due to the larger amount of carbon dioxide per 1,000 cubic meters to be removed in Laupichler's procedure. Laupichler's cost of about 20 cents per 1,000 cubic feet for making hydrogen from water gas indicates that the total cost of hydrogen when the Didier generator is used for water-gas production should be about 35 cents per 1,000 cubic feet.

The reports of the British Falmouth Subcommittee on Imperial Defence [175] and of the British Labour Party's Hall Committee [176] on the economics of synthetic fuels present the most reliable information on total costs of production. The following statements are abstracts of the Falmouth and the Hall reports prepared by Egloff.[177]

The Billingham plant was originally intended to deal with coal only and to have a rated output capacity of 100,000 tons (30,000,000 Imperial gallons or 36,000,000 United States gallons) of motor spirit. It was subsequently decided to include pro-

[174] Laupichler, F. G., *Gas World*, **105**, 71–4 (1936) ; *Chem. & Met. Eng.*, **43**, 122–6 (1936).

[175] Falmouth, Viscount (Chairman), *Rept. of the Committee of Imperial Defence, Subcommittee on Oil from Coal*, H.M.S. Office, London, 1938, 71 pp.

[176] Hall, G. H. (Chairman, Committee of Labour Party), *Labour's Plan of Oil from Coal*, Labour Publications Dept., London, 1938, 79 pp.

[177] Egloff, G., *Ind. Eng. Chem.*, **30**, 1091–104 (1938).

vision for the treatment of coal tars to the extent of 50,000 tons of petrol per annum, thus making the capacity 150,000 tons (45,000,000 Imperial gallons or 54,000,000 United States gallons) of petrol per annum.

The quantity of coal it was then expected would be required for the plant when in full operation was stated to be as follows:

Coal hydrogenation:	Tons
For processing *	150,000–200,000
For all other purposes (steam, power, hydrogen production, etc.)	300,000–350,000
	500,000
Tar-oil hydrogenation † for steam, power, hydrogen production, etc.	100,000
Total	600,000

* The exact quantity depends, among other things, on the ash and moisture content of the coal.

† In addition, about 60,000 tons of tar oils is required.

This gives for the coal hydrogenation 1 ton of petrol for each 1.5 to 2 tons processed or for each 5 tons of total coal used.

The spirit produced by the plant was of a high grade, and during the last few months (in 1938) an octane rating of 75 was achieved. This is a high standard for a straight or undoped petrol.

If a new hydrogenation plant were to be built it would have to be designed to use coal only, as supplies of creosote or low-temperature tar sufficient to provide for another mixed-coal and tar plant were not available. The plant would have a capacity of 150,000 tons of petrol, as Imperial Chemical Industries, Ltd., regarded this size as the minimum from an economic point of view.

The capital cost of such a plant (to include land, offices, site development and design charges, research charges essential for this new plant, working capital, interest during construction, and fees payable to the International Hydrogenation Patents, Ltd.) was estimated by Imperial Chemical Industries, Ltd., at £8,000,000 ($40,000,000), made up approximately as follows:

	Pounds	Dollars
Capital cost (plant, materials, etc.):		
General services and workshops	1,035,000	5,175,000
Boilers and power plant	1,570,000	7,850,000
Gas-making, purification, and compression	1,762,000	8,810,000
Hydrogenation plant and refinery	2,880,000	14,400,000
	7,247,000	36,235,000
Sundry charges (research during construction, working capital, International Hydrogenation Patents fee)	750,000	3,750,000
Total	7,997,000	39,985,000

The estimated results of operations on a new plant using these assumed costs are given at the top of the next page in two groups: the first deals with a calculation for depreciation of the plant on the basis of 20-year life with no provision for obsolescence; the second group is based on a charge for depreciation and obsolescence combined sufficient to write off the plant within 10 years.

On the basis of a new plant to hydrogenate coal, costing $40,000,000 for the production of 150,000 tons a year of motor fuel, the production cost per United States gallon would be about 15.6 cents on the basis of a plant life of 20 years, no obsolescence charges included. On the basis of writing off the plant in 10 years, including depreciation and obsolescence, the cost per gallon of motor fuel would be 19 cents.

The British Labour Party, working independently of the Imperial Defence com-

	20-Year Life		10-Year Life	
	Imperial Gallons	United States Gallons	Imperial Gallons	United States Gallons
	pence	cents	pence	cents
Assumed average realization price at works (assuming existing rate of preference of 8 pence [16 cents] per gallon)	12.00	20	12.00	20
Deduct:				
Works cost (including works overhead)	7.20	12	7.20	12
Works profit before providing for depreciation and obsolescence	4.8	8	4.8	8
Provision for depreciation at 5 percent	2.13	3.63	.....	......
Provision for depreciation and obsolescence at 10 percent	.....	.....	4.27	7.1
Profit after charging depreciation	2.67	4.45	.....	......
Profit after charging depreciation and obsolescence	.....	.....	0.53	0.967

mittee, came to the conclusion that gasoline from hydrogenation of coal "at the present time" would cost about 11 pence (22 cents) per imperial gallon, or 18 cents per United States gallon. The following is taken from the British Labour Party's report:

On the basis of their experimental work, Imperial Chemical Industries, Ltd., was led to believe that petrol could be produced by hydrogenation at a cost of 7 to 9 pence (14 to 18 cents an Imperial gallon or 11.67 to 15 cents per United States gallon), of which about 2 pence (4 cents) would be due to the cost of coal. The figure realized in practice has not been disclosed, but there was some reason to think that with a reasonable allowance for interest on capital and amortization the price stood in the neighborhood of 11 pence (22 cents) an Imperial gallon. The I. G. Farbenindustrie has been similarly reticent, but it has been learned from an authoritative source that their cost of producing petrol (from brown coal) has been 25 pfennigs a kilogram, which is about 11

pence (22 cents) an Imperial gallon (18.3 cents per United States gallon) at par.

The chairman of Imperial Chemical Industries, Ltd., Lord McGowan, had twice referred to the high cost of producing petrol at Billingham. In his speech at the company's annual meeting on April 29, 1937, he said:

For general commercial reasons it is not the practice of the company to disclose the financial results of any particular activity. All that I can say, therefore, in regard to the hydrogenation plant is that up to date it has not shown results which would justify its description as a good commercial proposition, even with the advantages of the existing customs duty, and without that protection, of course, the enterprise would be uneconomic.

In the House of Lords on July 14, 1937, he said:

Although the process is today in successful operation, it does not, even with the protection afforded by the British Hydrocarbon Oils Production Act, present a favorable opportunity for the investment of large sums of private capital. · · · Success from a commercial point of view in the synthetic production of petrol depends largely, as far as

the future is concerned, upon the policy of the government of the day.

Although the company has not disclosed its accounts, it is not difficult to form a rough idea of the principal items in the operating costs of a hydrogenation plant similar to that at Billingham. The men employed in the plant are largely skilled workers, and their wages will average about £3 15s ($19) a week. On this basis, the wages bill for 2,000 men will be £390,-000 ($1,950,000) a year; spread over an annual production of 45,000,000 Imperial gallons (54,000,000 United States gallons) of motor spirit, this amount is equivalent to 2.1 pence (4.2 cents) an Imperial gallon (3.5 cents per United States gallon). The cost of the raw materials—600,000 tons of coal, 50,000 tons of creosote, and 12,000 tons of low-temperature tar—can hardly be put, at current market values, at less than £500,000 ($2,500,000), equivalent to 2.7 pence (5.4 cents) an Imperial gallon (4.5 cents per United States gallon).

Imperial Chemical Industries, Ltd., constructed the Billingham plant out of its reserve funds, but in a calculation of the operating costs of the hydrogenation process it is necessary to allow interest on the capital expenditure. With a rate of 3.5 percent, at which the money could be raised with a government guarantee, the interest on £5,500,000 ($27,500,000) would amount to £192,500 ($962,500) a year, or 1.0 pence (2 cents) an Imperial gallon (1.67 cents per United States gallon).

It is difficult to know at what figure amortization of the plant should be reckoned. Imperial Chemical Industries suggests amortization in 10 years with compound interest at 2½ percent on the reserves provided. German authorities have taken the view that 10 years is an unnecessarily short period, and amortization in 15 years with compound interest at 2½ percent on reserves seems reasonable; on a capital of £5,500,000 ($27,500,000) this would absorb about £300,000 ($1,500,000) a year, or 1.6 pence (3.2 cents) an Imperial gallon (2.67 cents per United States gallon).

The total of these costs—wages, raw materials, interest on capital, and amortization—is £1,382,500 ($6,912,500) a year or 7.4 pence (14.8 cents) an Imperial gallon (12.3 cents per United States gallon).

These estimates may be checked by the reports, made by Sir David Rivett personally and by a committee of which he was chairman, to the Australian Government. Sir David Rivett's estimates were based on figures supplied to him by Imperial Chemical Industries and by German firms. His final calculations were made in terms of Australian currency, costs, and wages, but by using his own multipliers as dividers it is possible to reverse the procedure and reach the European figures on which he ultimately relies, figures that have not otherwise been made generally available. By this means it may be calculated that the cost of a hydrogenation plant to produce 150,000 tons of petrol annually from coal (not, as at Billingham, from coal and other materials) is £7,500,000 ($37,500,-000). If amortization takes place in 15 years and interest on capital is charged at 3.5 percent, the cost of petrol works out at 10.5 pence (21 cents) an Imperial gallon (17.5 cents per United States gallon); if amortization takes place in 10 years and interest on capital is charged at 6 percent, the cost of petrol will be 12.75 pence (25.5 cents) an Imperial gallon (21.25 cents per United States gallon).

With a reasonable allowance for amortization and interest on capital it seems fair, therefore, to say that petrol can be produced by hydrogenation (directly from

coal) for about 11 pence (22 cents) an Imperial gallon (18.3 cents per United States gallon).

The Imperial Defence Committee studied the Fischer-Tropsch process for the hydrogenation of carbon monoxide. Statements were furnished to the committee setting out particulars relating to the recommended size of plant, estimates of the capital and operating cost, the type and yield of products it was claimed could be produced, and estimated realization value of the products, etc. The following are examples of the sizes of plants and estimates of capital cost submitted to the committee:

KOGASIN-OIL YEARLY PLANT-CAPACITY COSTS

20,000-ton plant (including coke ovens)	£1,000,000	($5,000,000)
		to
	£1,500,000	($7,500,000)
35,000-ton plant:		
Including coke ovens	£1,901,000	($9,505,000)
Direct gasification of coal in water-gas plant	£1,717,000	($8,585,000)
60,000-ton plant (including coke ovens and distillation plant)	£3,100,000	($15,500,000)

The estimates of cost were prepared at different dates, based on information supplied by Ruhrchemie A.-G.

Until more information is available as to the most suitable methods of treating both the primary and secondary products that will give the best economic return in this country, it is obviously impossible to obtain any reliable data as to costs of production. One witness gave estimated figures of the average costs of production of marketable products from a 35,000-ton-per-annum plant which ranged from 12.75 to 15 pence an Imperial gallon (21.25 to 25 cents per United States gallon), according to the period allowed for amortization of the capital. The average realization price taken was 13 pence (21.7 cents per United

States gallon). Another informant stated that, on the basis of the best yields of products that he could then accept, the overall cost of the primary product would not have to exceed 10.5 pence (17.5 cents) and finished products an average of 12.75 pence per Imperial gallon (21.25 cents per United States gallon) if proceeds were to equal costs. He had not enough data to say whether such results were practicable. Generally, the evidence appears to indicate that the costs of production by the Fischer-Tropsch process are not likely to be less than those by a process for direct hydrogenation of coal.

The following is reported from the British Labour Party's report: The synthetic process, unlike direct hydrogenation of coal, can be operated in relatively small units. The economic unit was said to be a plant producing about 35,000 tons of primary products annually, or, if it included its own catalyst plant, about 60,000 tons of primary products annually. The committee were given estimates for synthetic plants of two types: Plant A was a self-contained plant, with its own coke ovens, designed to produce annually 35,000 tons (11,077,500 gallons) of primary products from bituminous coal. If the Diesel oil fraction were "cracked," it would yield 28,350 tons of motor spirit annually exclusive of subsidiary products. Plant B was a plant without coke ovens designed to operate in conjunction with a coal-distillation unit and to produce from the low-temperature coke 10,000 tons of synthetic products annually. It was difficult to assess the cost of a British plant from German experience, especially in view of recent wide fluctuations in the price of steel, and all estimates had to be accepted with caution. Plant A, it was stated, would cost about £1,900,000 ($9,500,000) to build, which, spread over the 35,000 tons of syn-

thetic products made annually, gave £54 ($270) per ton of annual production. (It is not possible to state so confidently the cost of a plant designed to make water gas directly from black coal, as such a plant has not yet been operated on a commercial scale, but it would probably be about £200,000 [$1,000,000] cheaper.) Plant B, it was stated, would cost 4,500,000 RM in Germany, which is equivalent to £225,000 ($1,125,000) at par—this is £22.5 ($125.50) per ton of annual production. When allowance was made for the omission of coke ovens, this was in substantial agreement with the estimate for Plant A. To make a fair comparison, a portion of the capital costs of the accompanying coal-distillation plant should be added to the capital costs of Plant B. Estimates of the overall cost of finished petrol depend greatly on interest charges and the time allowed for amortization. With coal supplied to the coke ovens at 18s 6d ($4.62) per ton and amortization in 15 years, interest at 3 percent and depreciation on three-quarters of the capital would amount to not less than 21 percent of the cost of production.

For a plant similar to Plant A, Sir David Rivett made two estimates for the Australian Government of the cost of finished petrol. With amortization in 10 years, compound interest at 2.5 percent on accumulated reserves, and a return of 3.5 percent on capital, he estimated the cost at 15.8 pence (31.6 cents) an Imperial gallon; with amortization in 15 years, compound interest at 3 percent on accumulated reserves, and a return of 3.5 percent on capital, he estimated the cost at 13.0 pence (26 cents) an Imperial gallon (21.67 cents per United States gallon). These figures are in terms of Australian currency and conditions. The comparable British figures would be about 12.1 pence (24.2 cents) an Imperial gallon (20.17 cents per United States gallon) and 10.0 pence (20 cents) an Imperial gallon (16.7 cents per United States gallon). These are about the same as the estimated costs of direct hydrogenation of coal.

For Plant B, the overall cost of the finished motor spirit was given as 20.21 pfennigs a kilogram, which works out at about 8 pence (16 cents) an Imperial gallon (13.3 cents per United States gallon) at par. The lower estimate for Plant B, compared with Plant A, results from the lower capital cost, which in turn is due to the absence of coke ovens; and for this, as already explained, some allowance should be made. When such allowance is made, the estimates are in substantial agreement.

The cost of gasoline production using natural gas at 3 to 5 cents per 1,000 cubic feet as raw material for a radically redesigned Fischer-Tropsch process was reported by Russell[178] to be close to the present cost of production of gasoline from petroleum. It is probable, however, that, when coal is the raw material, the cost will be considerably greater, but the use of cheap subbituminous coals or lignites and modern continuously operating gas generators may materially reduce the cost below that given by the British Committee Reports.[175, 176]

178 Russell, R. P., *Synthetic Liquid Fuels*— Hearings before a Subcommittee of the Committee on Public Lands and Surveys, United States Senate, Seventy-Eighth Congress, First Session, on S1243, August 3, 4, 6, 9, and 11, 1943. Government Printing Office, Washington, D. C., 1943, p. 39.

METHANOL SYNTHESIS FROM WATER GAS *

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Synthetic methyl alcohol or methanol produced by catalytic hydrogenation of carbon monoxide first appeared on the American market in 1923.[1] Domestic production began a few years later, and by 1933 the yearly production of methanol had reached almost 9,000,000 gallons and was valued at $1,680,000.[2] In 1940, methanol production reached a new high of about 45,000,000 gallons.[3]

Ipatieff is said to have been the first to prove that alumina could catalytically dehydrate alcohols to the corresponding olefins.[4] He also studied oxides of zinc, iron, and chromium and classified them as dehydrogenation catalysts.[5]

This work was followed by that of Sabatier and coworkers, who were able to arrange individual oxides in a series according to their ability to catalyze dehydration and dehydrogenation.[6] In 1905, they sug-

gested that methanol might be synthesized directly from carbon monoxide and hydrogen although they were never able to produce it in measurable quantities.[7]

In 1913, a basic patent, which broadly covered the process of synthesizing organic compounds from carbon monoxide and hydrogen,[8] was issued to the Badische Anilin und Soda Fabrik. This patent mentioned zinc and chromium oxides as constituents of catalysts used in the process. The first actual production[9] of methanol from hydrogen and carbon monoxide was disclosed in 1921 by Patart, Inspector General of the French Bureau of Explosives.[10] He was familiar with the Haber process for making ammonia from hydrogen and nitrogen and reasoned that at high pressures the equilibrium between hydrogen, carbon monoxide, and methanol would be displaced in the direction of methanol since there was a large reduction in volume during the reaction. Patart disclosed as catalytic agents all metals and their oxides and salts which are known to favor hydrogenations or oxidations. He fixed the tempera-

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1 Larson, A. T., *Trans. Electrochem. Soc.*, **71**, 346–51 (1937).

2 U. S. Bureau Census, *Statistical Abstract of United States, 1939*, p. 816.

3 *Chem. & Met. Eng.*, **48**, No. 2, 102 (1941).

4 Ipatieff, V. N., *J. Russ. Phys. Chem. Soc.*, **33**, 143–9, 632–43 (1901), **34**, 182–95 (1902).

5 Ipatieff, V. N., *Ber.*, **34**, 596–600 (1901), **35**, 1047–64 (1902), **36**, 1990–2003 (1903).

6 Sabatier, P., and Senderens, J. B., *Ann. chim. phys.*, (8), **4**, 319–432 (1905).

7 Larson, A. T., *Trans. Electrochem. Soc.*, **71**, 346–51 (1937).

8 Badische Anilin und Soda Fabrik, German Pat. 293,787 (1913).

9 Lormand, C., *Ind. Eng. Chem.*, **17**, 430–2 (1925).

10 Patart, G., Fr. Pat. 540,343 (1921).

ture range as 300 to 600° C and the pressure range as between 150 and 200 atmospheres. Sometime before the publication of the patent in 1922, Patart had operated a small experimental plant near Paris and made methanol using several catalysts.[9]

Although Patart first disclosed production of methanol from hydrogen and carbon monoxide, it is not surprising that the Badische Anilin und Soda Fabrik, which had developed the Haber ammonia process, was the first company to synthesize methanol commercially.[11] Badische's first patents covering the process appeared in 1923, and in that same year some of its synthetic methanol was sold in America.

The success of the Badische synthetic methanol process stimulated world-wide search for catalysts, and many synthetic methanol plants have been built to exploit the information gained in these researches.

Very little information has been published regarding the technical details of the many synthetic methanol plants in the world. Working pressures range from 150 atmospheres to almost 1,000 atmospheres; temperatures, from 250 to about 400° C.

General accounts giving various details of methanol synthesis have been published in four books.[12] The history of methanol synthesis has been reviewed by I. G. Farbenindustrie A.-G.[13] and by Lormand.[9] Papers reviewing the state of the art have

appeared frequently since 1925.[14] Five reviews of periodical and patent literature have also been published.[15] Transformation of coal into technical organic products such as methanol and higher alcohols has been discussed by numerous writers.[16]

Fieldner has concluded that use of off-peak water-gas capacity for methanol production is less favorable than full-time production of methanol.[17] Production of methanol from carbon monoxide and hy-

[11] Badische Anilin und Soda Fabrik, Brit. Pats. 227,147, 228,959, 229,714–5 (1923).

[12] Groggins, P. H., *Unit Processes in Organic Synthesis*, McGraw-Hill Book Co., New York, 2nd ed., 1938, pp. 469–73. Grignard, V., Dupont, G., and Locquin, R., *Traité de chimie organique*, Masson et Cie, Paris, 1937, Vol. 5, p. 826. Hilditch, T. P., and Hall, C. C., *Catalytic Processes in Applied Chemistry*, D. Van Nostrand Co., New York, 2nd ed., 1937, p. 115. National Research Council, *Twelfth Report of the Committee on Catalysis*, John Wiley & Sons, New York, 1940, pp. 120–4.

[13] I. G. Farbenindustrie A.-G., *Z. angew. Chem.*, **40**, 166 (1927).

[14] Anon., *Ind. Eng. Chem.*, **17**, 981–2 (1925). Fabre, R., *J. pharm. chim.*, (8), **2**, 113–7 (1925). Patart, G., *Bull. soc. encour. ind. nat.*, **137**, 141–73 (1925); *Chimie & industrie*, **13**, 179–85 (1925). Berr, R., *Brennstoff-Chem.*, **8**, 205–11 (1927). Voss, *Kunststoffe*, **17**, 79–80, 132–4, 205 7 (1927). Birck, E., and Nitzschmann, R., *Metallbörse*, **19**, 1350–1, 1 105–6, 1462–4, 1573–5, 1629–32, 1742 44, 1798–9, 1910–2 (1929). Ullrich, A., *ibid.*, **19**, 1181–2, 1238–9, 1294–5 (1929). Bodendorf, K., *Apoth. Ztg.*, **45**, 1141–4 (1930). Audibert, E., *Conférences-rapports sur les combustibles, Sec. Tchécoslovaque soc. chim. ind.*, 1930, 27 11; *Ann. combustibles liquides*, **5**, 239–72 (1930), **8**, 757 869 (1933). Dolgov, B. N., *J. Chem Ind.* (U.S S R.), **8**, 457–72 (1931). Fleury, M., *Mém. poudres*, **24**, 10–48 (1931). Simonet, R., *Peintures, pigments, vernis*, **8**, 1450 2, 1475–8 (1931). Pier, M., *Oel Kohle*, **1**, 47–53 (1933). Rosendahl, F., *Montan. Rundschau*, **25**, 1–14 (1933); *Petroleum Z.*, **29**, No. 6, 1–14 (1933). Sevast'yanov, Yu., *Khimstroi*, **6**, 112–20 (1934).

[15] Jaeger, A., *Ges. Abhandl Kenntnis Kohle*, **7**, 51–4 (1922–3). Dersin, H., *Chem.-tech. Rundschau*, **44**, 146 8, 176–8 (1928). Naphthali, M., *Gas u Wasserfach*, **72**, 1178–84 (1929). Löpmann, B., and Jaeckel, B., *Ber. Ges. Kohlentech.*, **4**, 1 20 (1931). Berkman, S., Morrell, J. C., and Egloff, G., *Catalysis*, Reinhold Publishing Corp, New York, 1940, 1129 pp.

[16] Muraour, H, *Recherches inventions*, **6**, 390–2 (1925). Patart, G., *Chimie & industrie*, **16**, 1713–29 (1926). Schick, F, *Braunkohle*, **24**, 1065–70 (1926). Berthelot, C., *Bull. soc. encour. ind. nat*, **126**, 485–511 (1927); *Proc. World Eng Congr.* (Tokyo), 1929, **32**, 309–38 (1931). Dunstan, A. E., and Shatwell, H. G., *J. Inst. Petroleum Tech.*, **14**, 64–77 (1928). Chaux, R., *Bull. soc chim.*, **43**, 385–411 (1928). Basore, C. A., *Mfrs.' Record*, **100**, No. 12, 29–30 (1931). Rogers, L. J., *Chem. Eng. Mining Rev.*, **23**, 373–80 (1931). Fanning, L. M., *Oil Gas J.*, **34**, No. 34, 142, 150 (1936).

[17] Fieldner, A. C., *Am. Gas J.*, **126**, 179–81 (1937).

drogen and from coke-oven gas has been discussed by Berthelot, Naudain, Osterreith and Dechamps, and Audibert.[18] The Badische, Patart, and Audibert processes have been compared by Elworthy,[19] and the economic possibilities of industrial ethyl alcohol and synthetic methanol as fuels for internal-combustion engines in France were reviewed by Kimpflin.[20] Some details of the manufacture of synthetic ethanol and methanol by the Mining Company of Béthune have been given by Damm.[21]

Ellis, Pier, and Bosch [22] have described the methanol and other high-pressure syntheses operated at the Leuna works of I. G. Farbenindustrie A.-G.

The Claude [23] process, which is reported to make methanol as a byproduct of ammonia synthesis, has been described by Claude, and Oshima [24] discussed the development and status of synthetic methanol and ammonia and compressed-gas industries in Japan in 1936. The du Pont synthetic ammonia and methanol plants have been described by Crane, Wardenburg, and anonymously,[25] and the Commercial Sol-

vents Corporation's methanol plant has been described by Woodruff, Gabriel, and Tropsch.[26] Production of methanol and Dry Ice from byproducts of the Groznenskii acetone-butyl alcohol factory have been described by Shvaitzer.[27]

DETERMINATION OF METHANOL EQUILIBRIUM

Larson [28] implied that the methanol equilibrium had been calculated with considerable certainty before attention was seriously turned to the synthesis of methanol from carbon monoxide and hydrogen and considered this knowledge of the equilibrium to have been in part responsible for the rapid technical success of the synthetic-methanol process. The earliest recorded work on the equilibrium was done in 1917-8 by Christiansen [29] but was not published until 1926. Synthetic methanol had been on the market for two years before the first published estimate of methanol equilibrium appeared.[30]

The equilibrium data published before 1932 on methanol have been summarized very well by Parks and Huffman.[31] To permit calculation of the equilibrium at various temperatures and pressures it was necessary to develop a general free-energy equation for the reaction:

18 Audibert, E., *Ann. combustibles liquides*, **8**, 757–869 (1933). Osterrieth, J. W., and Dechamps, G., *Gas J.*, **201**, 202–6 (1933); *Gas World*, **98**, No. 2531, Coking Sect., 14–7 (1933). Berthelot, C., *Chimie & industrie*, **37**, 211–23 (1937). Naudain, E., *Tech. ind. chim.*, No. 277, bis, 20–6 (1938).

19 Elworthy, R. T., *Can. Chem. Met.*, **9**, 139–40 (1925).

20 Kimpflin, G., *Rev. gén. sci.*, **39**, 700–3 (1928), **40**, 177–82, 211–5 (1929).

21 Damm, P., *Moniteur produits chim.*, **11**, No. 114, 1–5 (1928); *Chem. Zentr.*, **1928**, II, 2208.

22 Ellis, C., *Trans. Am. Inst. Chem. Engrs.*, **25**, 16–41 (1930). Pier, M., *Automobiltech. Z.*, **36**, 159–60 (1933). Bosch, C., *Chem. Fabrik*, **1934**, 1–10.

23 Claude, G., *Compt. rend.*, **182**, 877–81 (1926).

24 Oshima, Y., *Chem. Eng. Congr., World Power Conf.*, **1936**, advance proof No. G5, 10 pp.

25 Anon., *Ind. Eng. Chem.*, **22**, 433–7 (1930). Crane, J. E., *ibid.*, **22**, 795–9 (1930). Warden-

burg, F. A., *J. Franklin Inst.*, **221**, 449–64 (1936).

26 Woodruff, J. C., *Ind. Eng. Chem.*, **19**, 1147–50 (1927). Gabriel, C. L., *ibid.*, **20**, 1063–7 (1928). Tropsch, H., *Brennstoff-Chem.*, **9**, 1–2 (1928).

27 Shvaitzer, I., *J. Chem. Ind. (U.S.S.R.)*, **12**, 345–9 (1935).

28 Larson, A. T., *Trans. Electrochem. Soc.*, **71**, 346–51 (1937).

29 Christiansen, J. A., *J. Chem. Soc.*, **128**, 413–21 (1926); *J. Am. Chem. Soc.*, **52**, 3165 (1930).

30 Matignon, C., *Bull. soc. chim.*, **37**, 825–36 (1925).

31 Parks, G. S., and Huffman, H. M., *The Free Energies of Some Organic Compounds*, Chemical Catalog Co., New York, 1932, pp. 113–23.

$$CO + 2H_2 = CH_3OH(g)$$

Three methods of evaluating the integration constant in the free-energy equation have been used. Christiansen [29] in 1926 and Lacy and coworkers [32] in 1930 measured the equilibrium in the reactions:

$$2H_2 + HCOOCH_3 = 2CH_3OH(g)$$

$$CO + CH_3OH(g) = HCOOCH_3(g)$$
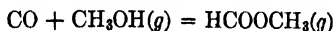
and calculated therefrom the equilibrium constant for the methanol reaction.

Numerous investigators have measured the methanol equilibrium directly at several temperatures and pressures.

The third law of thermodynamics has been applied to the available thermal data by a number of writers, and several estimates of the equilibrium have been made by means of the Nernst approximation.

Agreement among the equilibrium constants determined by the first two methods and estimates of it based on yields in the practical process were always fair, but for several years the values calculated from the third law of thermodynamics were 14 to 50 times as great as the experimental values.

Kelley [33] was the first to publish a free-energy equation for the methanol reaction. In deriving it, he used the entropy of liquid methanol at 298.1° K obtained by Parks.[34]

Smith and Francis [35] also published free-energy equations, using Parks' entropy of liquid methanol. Later Kelley [36] published a value for the entropy of liquid methanol, based on specific-heat measurements to

16° K of 30.3 ± 0.2 entropy units (E.U.) per mole at 298.1° K. This value was considerably lower than that of Parks, which had been based on measurements to only 90° K. Using his value for the entropy of methanol, Kelley [37] derived a new free-energy equation for the formation of methanol from hydrogen and carbon monoxide.

Equilibrium constants calculated from this equation were compared with constants based on the synthesis of methanol at high pressure by Lewis and Frolich,[38] Audibert and Raineau,[38] Brown and Galloway,[38] Morgan, Taylor, and Hedley,[38] and Fieldner and Brown [38] and with a constant determined at atmospheric pressure by Smith and Branting,[39] but in no case was the calculated equilibrium constant derived from the synthesis of methanol. Lacy, Dunning, and Storch,[32] Newitt, Byrne, and Strong,[40] von Wettburg and Dodge,[40] and Smith and Hirst [40] subsequently published experimental determinations of the equilibrium constant. These experimental equilibrium constants all agreed as to order of magnitude but were only one-tenth to one-fiftieth as large as the constants calculated from Kelley's equation. All the constants based on the third law of thermodynamics had been ob-

[32] Lacy, B. S., Dunning, R. G., and Storch, H. H., *J. Am. Chem. Soc.*, **52**, 926–38 (1930).

[33] Kelley, K. K., *Ind. Eng. Chem.*, **18**, 78 (1926).

[34] Parks, G. S., *J. Am. Chem. Soc.*, **47**, 338–45 (1925).

[35] Smith, D. F., *Ind. Eng. Chem.*, **19**, 801–3 (1927). Francis, A. W., *ibid.*, **20**, 283–5 (1928).

[36] Kelley, K. K., *J. Am. Chem. Soc.*, **51**, 180–7 (1929).

[37] Kelley, K. K., *Ind. Eng. Chem.*, **21**, 353–6 (1929).

[38] Audibert, E., and Raineau, A., *Ann. office combustibles liquides*, **3**, 367–428 (1928); *Rev. ind. min.*, **8**, Pt. I, No. 170, 286–314 (1928); *Ind. Eng. Chem.*, **20**, 1105–10 (1928). Brown, R. L., and Galloway, A. E., *ibid.*, **20**, 960–6 (1928). Fieldner, A. C., and Brown, R. L., *ibid.*, **20**, 1110–2 (1928). Lewis, W. K., and Frolich, P. K., *ibid.*, **20**, 285–90 (1928). Morgan, G. T., Taylor, R., and Hedley, T. J., *J. Soc. Chem. Ind.*, **47**, 117T (1928).

[39] Smith, D. F., and Branting, B. F., *J. Am. Chem. Soc.*, **51**, 129–39 (1929).

[40] Newitt, D. M., Byrne, B. J., and Strong, H. W., *Proc. Roy. Soc. (London)*, **A123**, 236–52 (1929). Von Wettburg, E. F., Jr., and Dodge, B. F., *Ind. Eng. Chem.*, **22**, 1040–6 (1930). Smith, D. F., and Hirst, L. L., *ibid.*, **22**, 1037–40 (1930).

tained using a value of 170,980 calories as the heat of combustion of liquid methanol as determined by Richards and Davis.[41]

Dodge[42] questioned this figure and pointed out that J. Thomsen's value for the heat of combustion of gaseous methanol at 18° C when corrected for the heat of vaporization would give 173,030 for the heat of combustion of liquid methanol at 18° C. Roth, in a communication to Smith,[43] gave 173,300 calories, which he determined for the heat of combustion of liquid methanol. Using Roth's value for the heat of combustion of liquid methanol and the other heat data as used by Kelley, Smith and Hirst[43] derived a free-energy equation which gave equilibrium constants that agreed fairly well with the experimental determinations mentioned above.

Rossini's[44] heats of combustion of methanol and carbon monoxide were used by Parks and Huffman[81] in deriving the free-energy equation below:

$$CO + 2H_2 = CH_3OH(g)$$
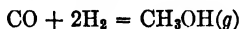
$$\Delta F° = 17,660 + 17.5T \ln T$$
$$- 0.0136T^2 - 57.2T$$

In 1934, Newton and Dodge[45] published further experimental determinations of the equilibrium constant and corrected all the previously published experimental constants for pressure by using the partial fugacity rule of Lewis and Randall.[46] When Newton and Dodge derived four free-energy equations using various combinations of the most accurate heat data, they found that the spread among equilibrium constants calculated from these equations was about half as great as that between the most divergent experimentally determined equilibrium constants after correction for pressure by the above method.

They considered the equation:

$$\log_{10} K_{p_0} = \frac{3,724}{T} - 9.1293 \log_{10} T$$
$$+ 0.00308T + 13.412$$

to be a satisfactory fit for the equilibrium data.

In 1936, Kassel[47] calculated entropies for gaseous methanol models having torsional oscillation and free rotation about the carbon monoxide bond by means of the available spectroscopic data. For the torsion model, the entropy was 56.74 E.U., and for the free-rotation model, 58.38. These values can be compared with that of 56.63 E.U. calculated from Kelley's entropy of liquid methanol. Thompson[48] stated in 1941 that it was certain that the free energy of gaseous methanol lies between the limits calculated by Kassel for the above models and gave for $-\left(\dfrac{F^0 - E_0^0}{T}\right)$ at 470° K a value of 52.365 which may be compared with Kassel's values of 52.196 and 53.350, respectively, for the torsion and free-rotation models.

The entropies of methanol as determined from low-temperature specific-heat measurements by Kelley and spectroscopic data by Kassel and Thompson are in substantial agreement, but the experimentally determined equilibrium constants for the methanol reactions vary widely among them-

41 Richards, T. W., and Davis, H. S., *J. Am. Chem. Soc.*, **42**, 1599–617 (1920).

42 Dodge, B. F., *Ind. Eng. Chem.*, **22**, 89–90 (1930).

43 Smith, D. F., and Hirst, L. L., p. 1039 of ref. 40.

44 Rossini, F. D., *J. Research, Natl. Bur. Standards*, **6**, 37–49 (1931), **8**, 119–39 (1932).

45 Newton, R. C., and Dodge, B. F., *J. Am. Chem. Soc.*, **56**, 1287–91 (1934).

46 Lewis, G. N., and Randall, M., *Thermodynamics*, McGraw-Hill Book Co., New York, 1923, pp. 225–7.

47 Kassel, L. S., *J. Chem. Phys.*, **4**, 493–6 (1936).

48 Thompson, H. W., *Trans. Faraday Soc.*, **37**, 254–5 (1941).

selves. This variation is not surprising, since the reaction has been carried out with a variety of catalysts on which numerous side reactions are known to occur. For instance, wherever the gases leaving the catalyst have been analyzed, it has been found that 2 volumes of hydrogen did not disappear for each volume of carbon monoxide. Formation of water and of oily liquids that float on methanol are frequently reported, and it has been shown that for a zinc oxide-chromium oxide catalyst [49] there are several reactions occurring at appreciable rates. It therefore seems that, until a catalyst specific for the methanol reaction is developed, the value of the equilibrium constant can be most accurately obtained by application of the third law of thermodynamics to the best available heat data or by calculation from the spectroscopic data.

METHANOL-PROCESS PATENTS

The process of synthesizing methanol from hydrogen and carbon dioxide gases in which the hydrogen is present in great excess has been patented by Edmonds,[50] but most methanol is made from gases containing hydrogen and carbon monoxide or mixed oxides of carbon. This process has been covered by numerous patents, among which can be listed those of Badische Anilin und Soda Fabrik,[51] Patart,[51] I. G. Farbenindustrie A.-G.,[51] Claude proc-

ess,[52] and the Commercial Solvents Corporation process.[53]

Blondelle [54] has patented a process in which a portion of the hydrogen required is derived from the action of steam on reduced iron oxide and the balance of the hydrogen and the required oxides of carbon are derived from the action of coke-oven gas on the iron oxide, the mixed resulting gases being cracked at 1,200° C and purified from sulfur before being passed over a copper catalyst activated by rare earths.

Humphrey [55] has patented a process of converting coal to methanol by the following steps. Coal is dried in a partly oxidizing atmosphere, then carbonized at low temperature; the semicoke is used to produce water gas, which is then passed over iron or other materials to produce higher paraffin hydrocarbons. The residual gases are then passed over methanol catalysts to produce methanol. Jaeger [56] claimed to have developed a process in which carbon monoxide and hydrogen react to form only formaldehyde, which, in a separate converter, without separation from the gas stream, is caused to react further with hydrogen in the presence of mild reduction and oxidation catalysts to produce methanol, but there is no report of successful commercial exploitation of this process.

GAS PRODUCTION AND PURIFICATION

Preparation of hydrogen and carbon monoxide, which are required in the synthesis of methanol, has been described in

49 Smith, D. F., and Hirst, L. L., ref. 40.

50 Edmonds, W. J., Can. Pat. 286,289 (1929). Edmonds, W. J., and Stengel, L. A., Can. Pat. 286,290 (1929). Edmonds, W. J., U. S. Pat. 1,875,714 (1932).

51 Badische Anilin und Soda Fabrik, Ger. Pat. 293,787 (1913); Brit. Pats. 229,714–5 (1923). Patart, G., Brit. Pats. 247,178 and 247,932 (1925). Pier, M., and Müller, C., Can. Pat. 241,483 (1925). I. G. Farbenindustrie A.-G., Brit. Pats. 308,181 (1927), 495,129 (1938). Pier, M., and Wietzel, G., U. S. Pat. 1,788,170 (1931).

52 Soc. l'air liquide, soc. anon. pour l'étude et l'exploitation des procédés G. Claude, Brit. Pat. 306,512 (1928).

53 Stengel, L. A., Can. Pat. 286,288 (1929); U. S. Pat. 1,754,371 (1930). Edmonds, W. J., and Stengel, L. A., U. S. Pat. 1,797,569 (1931).

54 Blondelle, R., U. S. Pat. 2,014,757 (1935).

55 Synthetic Ammonia and Nitrates, Ltd., and Humphrey, H. A., Brit. Pat. 282,578 (1927).

56 Jaeger, A. O., U. S. Pat. 1,824,896 (1931).

Chapters 36 and 39. The patents and articles below are listed because they have been granted to cover processes for producing gaseous mixtures, particularly for methanol synthesis. Coal may be distilled to produce synthesis gas,[57] and Natta[58] patented gasification of solid fuels or charcoal in gas producers held below 750° C when using not more than 1 volume of oxygen per 2 volumes of steam.

The cellular water-gas producer has been described by Heller,[59] and the Philipon gas producer and the installation at Sainte-Étienne has been described by Estival.[60] Takei[61] has described the use of natural coke briquets to make water gas for methanol and ammonia synthesis.

Gaseous hydrocarbons, such as methane, may be submitted to the action of an electric arc with the addition of a compound yielding oxygen, such as carbon dioxide or steam.[62]

Mixtures of carbon monoxide and hydrogen for the production of methanol and other oxygenated organic compounds are obtained by incomplete combustion of methane, which may be mixed with half its volume of oxygen and the mixture injected into a mass of coke maintained at about 1,000° C.[63]

A mixture of carbon monoxide and hydrogen for the production of methanol is obtained by passing over known catalysts a mixture of a hydrocarbon, such as methane, and carbon dioxide and steam, at temperatures between 600 and 1,200° C.[64]

Gaseous mixtures containing hydrocarbons are passed over catalysts like iron, cobalt, nickel, chromium, aluminum, manganese, silicon, carbon, copper, vanadium, and tungsten and compounds or mixed crystals of these elements together with superheated steam at temperatures of 1,000° C or higher to produce gaseous mixtures rich in hydrogen.[65]

Partial combustion of methane in admixture with steam of high temperature (for example, 1,300° C) followed by the addition of more steam and passage over a nickel catalyst at about 800° C has been patented for production of gas for methanol synthesis.[66]

Methane or other saturated hydrocarbons are converted to unsaturated hydrocarbons, hydrogen, and carbon oxides in two steps by treatment with oxygen or steam or both with or without a catalyst. After electric-arc heating or incomplete combustion, the gas is passed with steam over a catalyst containing nickel and aluminum oxide. Residual gases may be saturated with water vapor, preheated, subjected to partial combustion, then passed with additional steam over a nickel-magnesium catalyst to obtain an impure mixture of carbon monoxide and hydrogen, which may be freed from carbon dioxide and hydrogen sulfide and then used to make methanol.[67]

Mixtures of gases have been separated, with fractions suitable for ammonia or methanol synthesis, by absorption followed by fractional desorption on activated charcoal or silica gel.[68]

[57] Thau, A., *Z. Ver. deut. Ing.*, **82**, 129–38 (1938).

[58] Natta, G., Brit. Pat. 330,918 (1929) ; Fr. Pat. 681,147 (1929) ; Ger. Pat. 614,928 (1935).

[59] Heller, O., *Chimie & industrie*, Special No. 466–7, June, 1933.

[60] Estival, J., *Génie civil*, **109**, 405–7 (1937).

[61] Takei, M., *J. Fuel Soc., Japan*, **15**, 425–40 (in English 36–42) (1936).

[62] Soc. l'air liquide, Fr. Pat. 712,092 (1931).

[63] Patart, G., Brit. Pat. 247,176 (1925).

[64] Soc. anon. des charbons actifs Édouard Urbain, Fr. Pat. 641,195 (1927).

[65] Schulz, E. H., and Eisenstecken, F., Brit. Pat. 314,870 (1928).

[66] Chaffette, M., Fr. Pat. 733,248 (1932).

[67] I. G. Farbenindustrie A.-G., Brit. Pat. 269,547 (1926).

[68] British Celanese, Ltd., Finlayson, D., and Sharp, A. T., Brit. Pat. 365,092 (1930).

Claude [69] has described recovery of hydrogen-containing carbon monoxide from coke-oven-gas low-temperature fractionation.

Recovery of nitrogen, hydrogen, and carbon monoxide from residual coke-oven gases has been patented by Minotte.[70]

Crude hydrogen-nitrogen mixture for ammonia and methanol synthesis also may be recovered from coke-oven gases by condensation at low temperature and high pressure.[71]

Coke-oven gas may be subjected to oxidizing cracking at a high temperature in the presence of oxygen and the resulting gases subjected to low-temperature fractionation to prepare starting materials for ammonia and methanol synthesis.[72]

Modification of excess gases from blast furnaces to make them suitable for methanol and other syntheses has been patented.[73]

Residual gases from manufacture of hydrogen by the iron-steam process may be converted into a mixture of carbon monoxide, hydrogen, and nitrogen by bringing them into contact with coke heated externally to about 1,200° C.[74]

Hydrogen may be made by reaction of steam with reduced iron oxide and combined with the product from reduction of the iron oxide by coke-oven gas and the mixture cracked at high temperature.[75]

Gases containing a high percentage of inert gases (for instance, power gas containing carbon monoxide 15.3, hydrogen 30.6, nitrogen 51 percent) also may be used in methanol synthesis.[76]

Waste gases from coal, tar, or mineral-oil hydrogenation and from ammonia synthesis are used in the production of methanol.[77]

Use of gases containing a high percentage of inerts or a large excess of one of the reaction gases, with purging of some of the gas after passage over the catalyst and enrichment prior to the next passage over the catalyst, was covered in an early methanol patent.[78]

Treatment of phosphorus blast-furnace gases with steam to prepare methanol synthesis gases also has been patented.[79] .

GAS PURIFICATION

Sulfur and volatile iron compounds are poisons for some methanol catalysts, and numerous methods of removing them have been described. One of the earliest Badische patents [80] on the methanol synthesis stresses the necessity of exhaustive purification treatment of the synthesis gases to remove organic sulfur compounds and volatile iron compounds before passage over the methanol catalysts.

Substantially all the sulfur content of gases for methanol synthesis may be removed by passage of a gas mixture containing principally an oxide of carbon over iron at 400 to 850° C.[81]

Catalyst poisons, like volatile compounds of iron and sulfur compounds, are removed

[69] Claude, G., *Compt. rend.*, **182**, 877–81 (1926).

[70] Minotte, M. E. H., U. S. Pat. 1,875,253 (1932).

[71] Sakmin, P. K., *J. Chem. Ind. (U.S.S.R.)*, **13**, 1459–62 (1936); *Brennstoff-Chem.*, **18**, 69–71 (1937).

[72] Hans, J. E., Fr. Pat. 817,767 (1937).

[73] Soc. d'études et de construction metallurgiques, Fr. Pat. 683,615 (1929).

[74] Soc. des mines de Dourges, Fr. Pat. 706,504 (1930).

[75] Blondelle, R., U. S. Pat. 2,014,757 (1935).

[76] Pier, M., and Wietzel, G., U. S. Pat. 1,788,-170 (1931).

[77] I. G. Farbenindustrie A.-G., Fr. Pat. 684,-181 (1929).

[78] Badische Anilin und Soda Fabrik, Brit. Pat. 266,405 (1925).

[79] Voituron, E., Ger. Pat. 531,498 (1929).

[80] Badische Anilin und Soda Fabrik, Brit. Pat. 228,959 (1923).

[81] Bannister, Wm. J., U. S. Pat. 1,757,826 (1930).

from synthesis gases before they come into contact with the catalyst, one means men-. tioned being passage through a layer of active carbon.[82]

Sulfur is removed from synthesis gases by passage over one or more masses of zinc oxide with or without chromium oxide and then over more methanol catalysts sensitive to sulfur poisoning such as those containing copper or manganese or their compounds.[83]

Water gas and like mixtures of carbon monoxide and hydrogen to be used in the manufacture of methanol are given preliminary purification by treatment with steam in the presence of a catalyst promoting the production of hydrogen and carbon dioxide from carbon monoxide and steam. During this treatment, the organic sulfur compounds in the gas mixture are transformed to hydrogen sulfide, which is removed with the carbon dioxide.[84]

Gases containing carbon dioxide, hydrogen, and nitrogen made from residual gases from the manufacture of hydrogen from the iron-steam process are desulfurized by passage over a catalyst of reduced cupric oxide followed by washing in an alkaline solution or by passage over ferrous oxide followed by washing.[85]

Gases circulated in a process can be purified by passing them in rapid concurrent flow with a liquid absorbent which removes only a small proportion of the undesired constituents.[86]

High-boiling hydrocarbons or phenols or their mixtures at 10 atmospheres or higher pressure and at such a temperature that the concentration of hydrogen sulfide amounts to less than 0.3 percent by volume of the gas can be used to remove volatile sulfur compounds from the gases intended for the manufacture of ammonia and methanol.[87]

APPARATUS FOR METHANOL SYNTHESIS

The synthesis of methanol from carbon monoxide and hydrogen has necessitated equipment to withstand high operating pressures at fairly elevated temperatures. Problems of heat exchange have been severe because the reaction is exothermic. In consequence, there are numerous patents covering special high-pressure equipment developed to facilitate the operation of the synthesis.[88]

Maxted[89] has discussed the employment of high pressures in chemical industry and has given details about joints, shaft packing, internal heaters, and thermocouple leads.

Tongue[90] has written an excellent book on the design and construction of the high-pressure chemical plant. In a later book on chemical engineering he has devoted a chapter to pressure vessels for the chemical industry.[91] Newitt[92] has also pub-

[82] I. G. Farbenindustrie A.-G., Ger. Pat. 462,-837 (1928). Pier, M., Mueller-Cunradi, M., Wietzel, G., and Winkler, K., U. S. Pat. 1,766,763 (1930).

[83] Dreyfus, H., Brit. Pat. 335,962 (1929) ; U. S. Pat. 1,868,096 (1932).

[84] Wietzel, G., and Winkler, K., Ger. Pat. 488,-156 (1923).

[85] Soc. des mines Dourges, Fr. Pat. 706,504 (1930).

[86] Gordon, K., and Imperial Chemical Industries, Ltd., Brit. Pat. 432,574 (1935).

[87] I. G. Farbenindustrie A.-G., Brit. Pat. 336,-319 (1929).

[88] Soc. nationale de recherches sur le traitement des combustibles, Fr. Pat. 699,438 (1929). Edmonds, W. J., Can. Pats. 309,962-3 (1930) ; U. S. Pat. 1,848,466 (1932). Audibert, E., U. S. Pat. 1,870,665 (1932). Troitskii, K. V., Russ. Pats. 44,239 (1935), 51,150 (1937).

[89] Maxted, E. B., J. Soc. Chem. Ind., 45, 366-70T (1926).

[90] Tongue, H., The Design and Construction of High Pressure Chemical Plant, Chapman and Hall, London, 1934, 420 pp.

[91] Tongue, H., A Practical Manual of Chemical Engineering, D. Van Nostrand Co., New York, 1939, pp. 178–241.

[92] Newitt, D. M., The Design of High Pres-

lished a useful book on the design of high-pressure plants and the properties of fluids at high pressures.

Various systems and devices have been patented for exchanging heat between reactants and reacted gases or for raising the reactants to the required temperatures.[93] Converters and methods of arranging catalysts in them have been patented.[94] Use of zinc or alloys of zinc, of cadmium, of steel containing a high percentage of chromium, and of metals or alloys resistant to carbon monoxide as lining or construction materials for methanol converters has been patented.[95]

It has been claimed that corrosion of steel during the synthesis of methanol results mainly from the production of iron carbonyl. Metals alloyed with steel can reduce the formation of carbonyl. The most resistant steels are those with high chromium content (13 to 15 percent). Chrome-vanadium steel has been reported to be unsuitable from the standpoint of corrosion.[96]

Use of a layer of nonreducing gases, such as nitrogen or carbon dioxide, to prevent contact of the copper walls of the catalyst chamber with reducing gases, which tend to diffuse through copper by reduction of oxide, has been patented.[97] Reaction in the pores of a wall between reactants supplied individually to either side of the wall has been patented.[98] Introduction of the fresh gases into the circuit through an injector nozzle to circulate the reacting gases also has been patented.[99] Patents have been issued on the suspension of the catalyst throughout the reaction space and whirling by a current of gas in synthesis of methanol.[100] Undesired side reactions may be avoided by injecting the liquid reaction product continuously or from time to time directly into the contact mass.[101]

In exothermic syntheses, such as methanol from carbon monoxide and hydrogen, a liquid such as water is added to the reaction gases to control the temperature of the reaction,[102] or the gas is introduced in predetermined amounts to separated portions of different content of catalyst while continuous gas circulation is maintained.[103]

PURIFICATION OF METHANOL

Purity of methanol varies with the selectivity of the synthesis catalyst. Sometimes esters and ethers and oily, high-molecular-weight substances are produced. The methods of purification employ centrifug-

sure Plant and the Properties of Fluids at High Pressures, Oxford University Press, London, 1940, 491 pp.

93 Almquist, J. A., Brit. Pat. 344,576 (1928). Gordon, K., and Imperial Chemical Industries, Ltd., Brit. Pat. 317,131 (1928). Brill, J. L., Brit. Pat. 342,854 (1928). Morgan, G. T., and Tongue, H., Brit. Pat. 325,678 (1929). Casale, L., U. S. Pat. 1,790,853 (1931). Chaffaut, R. D., U. S. Pat. 1,942,021 (1934). Edmonds, W. J., U. S. Pat. 1,980,718 (1935). Gavrilow, V. S., Russ. Pats. 44,238, 44,240 (1935). Kleinschmidt, R. V., U. S. Pat 2,051,774 (1936).

94 Patart, G. L. E., Brit. Pat. 252,362 (1925). Pyzel, E., U. S. Pat. 2,006,078 (1935).

95 Pier, M., Rumpf, W., Lappe, F., and Stern, G., Can. Pat. 254,987 (1925). I. G. Farbenindustrie A.-G., Brit. Pats. 341,153 (1929), 454,-428 (1936); Fr. Pat. 799,270 (1936). Pier, M., U. S. Pat. 1,823,468 (1931).

96 Ivanov, K. N., and Kozlov, L. I., Khim. Mashinostroenie, 5, No. 6, 86-9 (1936); Chimie & industrie, 38, 923 (1936).

97 I. G. Farbenindustrie A.-G., Brit. Pat. 260,-888 (1926).

98 Verein für chemische Industrie A.-G., Swiss Pat. 127,243 (1926); Ger. Pat. 474,283 (1927).

99 Casale, L., Brit. Pat. 252,573 (1925); Can. Pat. 267,008 (1926).

100 I. G. Farbenindustrie A.-G., Brit. Pat. 274,-904 (1926); Fr. Pat. 638,109 (1927).

101 Pier, M., Ger. Pat. 484,166 (1923).

102 Compagnie de Béthune, Fr. Pat. 639,058 (1927); Brit. Pat. 283,499 (1927).

103 Richardson, R. S., U. S. Pat. 1,921,776 (1933).

ing,[104] oxidation and rectification,[105] solvent washing with solvents scarcely miscible with aqueous methanol and having lower boiling points (such as carbon disulfide or benzine),[106] or distillation to remove ethers and esters.[107]

Crude methanol can be purified by heating to 100 to 300° C at pressures above 50 atmospheres in the presence of oxygen-containing compounds that are not reduced to the metallic state under the conditions of working or in the presence of sulfur-containing compounds of the heavy metals of the first, second, fourth, fifth, sixth, or eighth groups.[108] Higher-molecular-weight alcohols can be converted into sulfuric acid esters or their salts by treatment with sulfuric acid and oleum.[109]

Methanol and other alcohols boiling below 100° C may be treated with a halogen, such as chlorine or bromine, in a quantity less than that required to satisfy the "unsaturated value" of the alcohol; the material is then distilled, treated with alkali to remove halogen acid, and fractionated.[110] Organic liquids prepared catalytically from hydrogen and oxides of carbon may also be purified by treatment with bases.[111] The heat of the reaction mixture coming from the catalysis chamber has been utilized for the distillation and rectification of the crude liquid product obtained by the process.[112] Methanol may also be purified by treatment with a salting-out solution and a solvent for hydrocarbons which is substantially immiscible with the mixture of methanol and salting-out solution.[113]

CATALYSTS FOR SYNTHESIS OF METHANOL

A great number and wide variety of methanol catalysts have been patented or described in the literature. A good methanol catalyst should give high conversion of the synthesis gases to methanol with as little as possible conversion to side reaction products, such as methane, ethers, and higher alcohols. It should also be capable of maintaining high activity for long periods and should be relatively insensitive to poisons, such as sulfur compounds. A catalyst that is active at lower temperatures has another advantage, since, at a given pressure, the equilibrium amount of methanol in the gas mixture increases as the temperature is lowered.

Two general methods of testing materials as methanol catalysts have been widely used. Decomposition of methanol vapor on the materials being tested as catalysts at atmospheric pressure and temperatures in the range of 250 to 400° C has been extensively employed as a rapid and inexpensive means of evaluating methanol catalysts. For more precise testing of catalysts believed to show considerable promise, carbon monoxide and hydrogen mixtures are passed over the catalyst at elevated temperatures and pressures, and the weight of methanol formed is determined.

The literature on the thermal decomposition of methanol by various contact substances was reviewed by Schellenberg,[114]

104 Giesen, J., Hanisch, H., and Dally, M., U. S. Pat. 2,115,553 (1938).

105 Nikitin, V. M., J. Chem. Ind. (U.S.S.R.), 14, 1067–72 (1937).

106 Scheuble, R., U. S. Pat. 2,083,125 (1937).

107 Fel'dman, Y. A., and Allison, E., J. Chem. Ind. (U.S.S.R.), 12, 1237–40 (1935).

108 I. G. Farbenindustrie A.-G., Fr. Pat. 746,-640 (1933).

109 Deutsche Hydrierwerke A.-G., Ger. Pat. 535,853 (1929).

110 Imperial Chemical Industries, Ltd., and Armit, J. W., Brit. Pat. 346,658 (1929).

111 I. G. Farbenindustrie A.-G., Ger. Pat. 542,-616 (1923).

112 Soc. Italina ricerche industriali, Fr. Pat. 660,108 (1928).

113 Ward, M. J. V., and Imperial Chemical Industries, Ltd., Brit. Pat. 309,708 (1928).

114 Schellenberg, A., Ges. Abhandl. Kenntnis Kohle, 7, 9–12 (1922–3).

but since that time a great amount of work has been done.

Frolich [115] and coworkers were the first to show that there is definite relationship between the synthesis of an alcohol from carbon monoxide and hydrogen and its decomposition over the same catalyst combinations at atmospheric pressure. In this work the catalysts were cupric oxide-zinc oxide and zinc oxide-chromic oxide, and it was concluded that agreement between decomposition and synthesis experiments was so close that the inexpensive decomposition method was suitable for evaluating catalysts for high-pressure synthesis.

Huffman and Dodge [116] worked with a series of zinc oxide-chromic oxide catalysts at 350° C and obtained good but not complete parallelism between decomposition and synthetic activity of these catalysts. For catalysts containing 60 to 100 percent chromic oxide, they found very little activity for decomposition into carbon monoxide and hydrogen, whereas these catalysts had considerable synthetic activity at high pressure. Storch [117] obtained still less parallelism between decomposition and synthetic activity when he used some zinc oxide-chromic oxide catalysts. He found that the catalyst containing about 90 percent zinc oxide and 10 percent chromic oxide was more active in synthesis at about 200 atmospheres pressure than either pure zinc oxide or pure chromic oxide, whereas in decomposition experiments at atmospheric

pressure these materials showed no appreciable differences in activity.

Most of the reviews of the technical and patent literature on methanol synthesis devote considerable time to catalysts. Jaeger [118] reviewed the general literature to 1923 and Dersin [119] to 1929; Löpmann and Jaeckel [120] reviewed the German patent situation on catalysts, gas purification, equipment, and product purification to 1931. Mittasch [121] has reviewed development of complex catalysts.

Almquist [122] has given a brief account of catalysts to 1926, and Mitchell [123] has surveyed the methanol process in more detail.

Audibert [124] has reviewed commercial synthesis of methanol and paid much attention to side reactions and catalysts. Pascal [125] reviewed synthesis of methanol in a general article on hydrogenation and cracking, and the role of the suboxides in methanol and other syntheses from hydrogen and carbon monoxide has been reviewed by Audibert.[126]

In *Catalysis* by Berkman, Morrell, and Egloff [15] methanol catalysis is considered frequently and methanol-synthesis catalysts are tabulated on pages 685 to 689; catalytic hydrogenation of carbon monoxide is also considered on pages 813 and 814.

Zinc oxide has been patented as a metha-

[115] Frolich, P. K., *J. Soc. Chem. Ind.*, **47**, 173-9T (1928). Frolich, P. K., Fenske, M. R., Taylor, P. S., and Southwick, C. A., Jr., *Ind. Eng Chem.*, **20**, 1327-30 (1928). Cryder, D. S., and Frolich, P. K., *ibid.*, **21**, 867-71 (1929). Fenske, M. R., and Frolich, P. K., *ibid.*, **21**, 1052-5 (1929). Frolich, P. K., *Trans. Electrochem. Soc.*, **71**, 317 (1937).

[116] Huffman, J. R., and Dodge, B. F., *Ind. Eng. Chem.*, **21**, 1056-61 (1929).

[117] Storch, H. H., *J. Phys. Chem.*, **32**, 1743-7 (1928).

[118] Jaeger, A., *Ges. Abhandl. Kenntnis Kohle*, **7**, 51-4 (1922-3).

[119] Dersin, H., *Chem.-tech. Rundschau*, **44**, 146-8, 176-8 (1929).

[120] Löpmann, B., and Jaeckel, B., *Ber. Ges. Kohlentech.*, **4**, 1-20 (1931).

[121] Mittasch, A., *Z. Elektrochem.*, **36**, 569-80 (1930).

[122] Almquist, J. A., *J. Chem. Education*, **3**, 385-9 (1926).

[123] Mitchell, J. A., *ibid.*, **9**, 59-71 (1932).

[124] Audibert, E., *Ann. combustibles liquides*, **6**, 655-709 (1931).

[125] Pascal, P., *Tech. moderne*, **17**, 449-56 (1925).

[126] Audibert, E., *Chimie & industrie*, **13**, 186-94 (1925).

nol catalyst many times,[127] and studies of methanol synthesis with zinc oxide catalysts prepared in a variety of ways have been made by several investigators.[117, 128] Activity of this catalyst depends particularly on its pretreatment. Hüttig, Kostelitz, and Feher [129] made thirty preparations of zinc oxide, decomposed methanol on them, and concluded that particularly active catalysts resulted when zinc carbonate was decomposed in an atmosphere of steam or methanol, or from the combustion of zinc wool, or from thoroughly washed zinc hydroxide precipitates.

Kostelitz, Hüttig, and Kittel [130] compressed basic zinc carbonates to pressures of 50 to 5,000 atmospheres, then converted them to zinc oxide and determined their activity in the decomposition of methanol. They concluded that, on a weight basis, decomposition decreased with increased compression, but on a volume basis it increased. Several complex zinc oxalates were decomposed to give methanol catalysts,[131] and it was concluded that those oxalates that were most tightly bound yielded most-active methanol decomposition catalysts.

Ivannikov, Frost, and Shapiro [128] decomposed zinc oxide hydrates at temperatures from 100 to 1,300° C and concluded that the activity of the resulting zinc oxide, where used as a methanol decomposition catalyst, decreased sharply as the decomposition temperature was raised. They also found that the decrease in activity began sooner and proceeded more rapidly than the decrease in surface caused by sintering.

Hüttig, Strial, and Kittel [132] prepared numerous chromic oxide catalysts and tested them for decomposition of methanol. They concluded that differences in activity were not due solely to changes in area but mainly to differences in atomic and molecular arrangements in the surface.

Copper is a favorite lining material for methanol catalyst chambers, and many catalysts containing copper as a major ingredient have been patented and investigated.[133] Catalysts containing copper in sizable amounts are characterized by Larson [28] and Lazier [134] as very active in the synthesis of methanol at low temperatures but as tending to catalyze side reactions, such as methane formation, which is followed by runaway temperatures and subsequent loss of catalytic activity.

Audibert [135] considered copper made by

127 Badische Anilin und Soda Fabrik, Ger. Pat. 293,787 (1913). Dreyfus, H., Brit. Pat. 262,-494 (1925) ; U. S. Pat. 1,738,989 (1929). I. G. Farbenindustrie A.-G., Brit. Pat. 257,256 (1925). Bloomfield, G., U. S. Pat. 1,668,838 (1928). Natta, G., Fr. Pat. 670,763 (1929) ; Swiss Pat. 140,093 (1929) ; U. S. Pat. 1,815,677 (1935) ; Brit. Pat. 330,919 (1929) ; Fr. Pat. 822,818 (1938). Bader, W., and Green, S. J., U. S. Pat. 1,793,350 (1931). Krauch, C., and Pier, M., Ger. Pat. 671,606 (1939).

128 Patart, G., Compt. rend., 179, 1330- 2 (1924). Morgan, G. T., Taylor, R., and Hedley, T. J., J. Soc. Chem. Ind., 47, 117-22T (1928). Frolich, P. K., Fenske, M. R., Taylor, P. S., and Southwick, C. A., Ind. Eng. Chem., 20, 1327–30 (1928). Brown, R. L., and Galloway, A. E., ref. 38. Cryder, D S., and Frolich, P. K., ref. 115. Berl, E., and Bemmann, R., Z. angew. Chem., 44, 84–9 (1931). Lazier, W. A., and Vaughen, J. V., J. Am. Chem. Soc., 54, 3080–95 (1932). Ivannikov, P. Ya., Frost, A. V., and Shapiro, M. I., Compt. rend. acad. sci. (U.R. S.S.), 1933, 124–6. Molstad, M. C., and Dodge, B. F., Ind. Eng. Chem., 27, 134–40 (1935).

129 Hüttig, G. F., Kostelitz, O., and Feher, I., Z. anorg. allgem. Chem., 198, 206–18 (1931).

130 Kostelitz, O., Hüttig, G. F., and Kittel, H., Z. Elektrochem., 39, 862–8 (1933).

131 Hüttig, G. F., and Goerk, H., Z. anorg. allgem. Chem., 231, 249–63 (1927).

132 Hüttig, G. F., Strial, K., and Kittel, H., Z. Elektrochem., 39, 368–73 (1933).

133 Badische Anilin und Soda Fabrik, Brit. Pat. 227,147 (1923). Krauch, C., and Pier, M., Ger. Pat. 671,606 (1939).

134 Twelfth Report of the Committee on Catalysis, ref. 12.

135 Audibert, E., Tech. moderne, 20, 861–6 (1928). Audibert, E., and Raineau, A., Ind. Eng. Chem., 20, 1105–10 (1928).

reducing copper oxide more active than zinc oxide and suitable for use at lower pressures.

Numerous copper oxide base catalysts were patented by Storch.[136] They consisted of copper obtained by decomposition of a cuprammonium compound followed by reduction with hydrogen; copper with a fluoride of calcium, barium, strontium, or magnesium; and cupric oxide precipitated from a cuprammonium salt solution in intimate mixture with magnesium hydroxide.

Audibert[137] has patented a copper catalyst prepared from copper nitrate or an organic copper salt by alkali precipitation, washing, drying *in vacuo*, mixing with a small proportion of violet copper, and finally reducing at 200° C or lower with hydrogen or carbon monoxide.

Plotnikov[138] and Kaganova found that pure copper catalyst made from Kahlbaum's and Merck's copper oxides were quite different in length of activity. They also found the addition of 6 mole percent of vanadium pentoxide to give a catalyst which decomposed methanol completely, but gave carbon dioxide and methane as well as hydrogen and carbon monoxide.

One of the most active and rugged types of methanol catalysts consists of combinations of zinc and chromium oxides.[28, 134] Such a combination is covered in one of the earliest Badische Anilin und Soda Fabrik[139] methanol patents, which claimed use of catalysts containing at least one of the hydrogenating elements—zinc—associated with one or more of the elements or their compounds—chromium—and free from the

alkali metals and iron, nickel, or cobalt. Many later patents[140] claim various combinations of zinc and chromium oxides. Taylor and Kistiakowsky[141] on measuring absorptions of hydrogen, carbon monoxide, and carbon dioxide on zinc oxide and zinc oxide-chromic oxide at 0 and 100° C found that the mixed oxide catalyst had a greater absorptive capacity than the zinc oxide. Extensive studies of methanol decomposition on zinc oxide-chromic oxide catalysts have been made.[116, 117, 142] Mixed oxides in the proportion of about 4 atoms of zinc to 1 of chromium give a catalyst that is more active than either zinc oxide or chromic oxide or any other combination of them in decomposing methanol into carbon monoxide and hydrogen. When used for synthesis by Cryder and Frolich[115] and Huffman and Dodge[116] the catalyst of that composition was also most active in formation of methanol from carbon monoxide and hydrogen. Storch,[117] however, found little difference in decomposition activity of the pure oxides and a mixture contain-

[140] Patart, G., Brit. Pats. 247,932, 252,361 (1925) ; U. S. Pats. 1,836,085 (1931), 1,859,244 (1932). Mittasch, A., Winkler, K., and Pier, M., Can. Pat. 251,484 (1925) ; U. S. Pat. 1,558,-559 (1925). Synthetic Ammonia and Nitrates, Ltd., and Smith, H. G., Brit. Pat. 275,345 (1926). Synthetic Ammonia and Nitrates, Ltd., and Franklin, R. G., Brit. Pats. 290,399, 293,056 (1926). Imperial Chemical Industries, Ltd., Fr. Pats. 642,318, 644,189, 689,757 (1927). Smith, H. G., Franklin, R. G., and Imperial Chemical Industries, Ltd., Brit. Pat. 316,113 (1928). Lazier, W. A., and Zeisberg, F. C., Brit. Pat. 313,098 (1928). British Celanese, Ltd., Bader, W., and Thomas, E. B., Brit. Pat. 345,649 (1929). Franklin, R. G., U. S. Pats. 1,774,432 (1930), 1,878,390 (1932). Kauzner, A., Swiss Pat. 150,613 (1930). Ikawa, K., Japan. Pat. 91,310 (1931). Lusby, O. W., U. S. Pat. 1,900,-828 (1933). Lazier, W. A., U. S. Pat. 1,984,884 (1934).

[141] Taylor, H. S., and Kistiakowsky, G. B., *J. Am. Chem. Soc.*, **49**, 2468–76 (1927).

[142] Smith, D. F., and Hawk, C. O., *J. Phys. Chem.*, **32**, 415–24 (1928). Cryder, D. S., and Frolich, P. K., ref. 115.

[136] Storch, H. H., U. S. Pats. 1,681,750–2 (1928), 1,708,460, 1,738,971 (1929), 1,875,273 (1932) 1,937,728 (1933).

[137] Audibert, E., Brit. Pat. 271,538 (1926).

[138] Plotnikov, V. A., and Kaganova, E. M., *J. Chem. Ind. (U.S.S.R.)*, **7**, 672–4 (1930).

[139] Badische Anilin und Soda Fabrik, Brit. Pat. 229,715 (1923).

ing 90 atomic percent of zinc but a considerably greater synthesis activity for the mixture. Plotnikov and Ivanov [143] also studied decomposition of methanol on a zinc oxide-chromic oxide catalyst, and Kostelitz [144] has prepared a number of such catalysts and studied decomposition of methanol on them at several temperatures from 300 to 360° C. When using a 4 ZnO-Cr_2O_3 catalyst at 250 atmospheres and 370° C, Dolgov and Karpov [145] had conversions of 90 percent per pass with a total yield of 63 percent of methanol. Veltistova, Dolgov, and Karpov [146] have prepared 8 ZnO-1.5 Cr_2O_3 and obtained a yield 1.2 kilograms of methanol per hour per liter of catalyst at 390 to 400° C and 250 atmospheres. Sulfur compounds must be removed from the gas.

Molstad and Dodge [128] studied mixtures of zinc and chromium oxides made by ammonia precipitation from a solution of the mixed nitrates and found them active, rugged methanol catalysts. In a short-time test the most active was the mixed oxides consisting of 25 atomic percent chromium and 75 atomic percent zinc, but they found that catalysts containing more chromium increased in activity during tests and that the improvement was accelerated by temperatures up to 100° C above the maximum activity temperature. They considered the best catalyst for long service to be that containing zinc and chromium in equal atomic percentages, which produced almost pure methanol and was unaltered by long use at considerably above normal operating temperatures. Their conclusion from the short-time tests, that the mixed oxides consisting of 25 atomic percent chromium and 75 atomic percent zinc had greater activity, is in agreement with the widely claimed necessity that zinc be in excess,[147] while the greater long-time activity they found for the catalyst with chromium in excess agrees with the claims in several patents.[148]

Molstad and Dodge compared the activity of the zinc-chromium oxide catalysts they prepared from trivalent chromium by ammonia precipitation from a solution of the nitrate with those prepared from hexavalent chromium by other investigators [149] and concluded that their catalysts were two to three times as active as those of similar composition prepared from hexavalent chromium or from trivalent chromium by ignition of the oxalate. The Molstad and Dodge catalysts permitted inlet space velocities in the range of 25,000 to 50,000 at working temperatures in the range of 300 to 400° C and gave conversions per pass of 17 to 25 percent of the carbon monoxide to methanol.

Promotion of zinc oxide-chromium oxide catalysts has been studied by Dolgov and

143 Plotnikov, V. A., and Ivanov, K. N., *J. Chem. Ind. (U.S.S.R.)*, **6**, 940-3 (1929).

144 Kostelitz, O., *Kolloid-Beihefte*, **41**, 58-72 (1934).

145 Dolgov, B. N., and Karpov, A. Z., *Khim. Tverdogo Topliva*, **3**, 282-8 (1932).

146 Veltistova, M. V., Dolgov, B. N., and Karpov, A. Z., *J. Chem. Ind. (U.S.S.R.)*, **11**, No. 9, 24-32 (1934).

147 Mittasch, A., Winkler, K., and Pier, M., Can. Pat. 251,484 (1925) ; U. S. Pat. 1,558,559 (1925). Patart, G., Brit. Pat. 252,361 (1925). Synthetic Ammonia and Nitrates, Ltd., and Smith, H. G., Brit. Pat. 275,345 (1926). Imperial Chemical Industries, Ltd., Fr. Pat. 689,-757 (1927). Franklin, R. G., U. S. Pat. 1,774,-432 (1930). Plotnikov, V. A., and Ivanov, K. N., *J. Chem. Ind. (U.S.S.R.)*, **7**, 1136-45 (1930). Ivanov, K. I., and Gusev, V. I., *ibid.*, **12**, 1143-6 (1935).

148 Lazier, W. A., and Zeisberg, F. C., Brit. Pat. 313,093 (1928). Lusby, O. W., U. S. Pat. 1,900,829 (1933). Lazier, W. A., U. S. Pat. 1,984,884 (1934).

149 Morgan, G. T., Taylor, R., and Hedley, T. J., ref. 38. Brown, R. L., and Galloway, A. E., ref. 38. Cryder, D. S., and Frolich, P. K., *J. Soc. Chem. Ind.*, **47**, 176T (1928). Lazier, W. A., and Vaughen, J. V., ref. 128.

Karpinskiĭ,[150] who found that 1 percent of thorium dioxide, zirconium dioxide, and tantalum oxide were most effective in increasing the yield of methanol. Other varieties of zinc oxide-chromium oxide catalyst have been prepared.[146]

It has been said that the presence of lead and copper in the zinc-chromium oxide catalyst lowers its productivity somewhat and that more than 1 percent of sulfide or sulfate sulfur lowers the productivity and increases the amounts of esters in the product. As little as 0.1 percent of iron has been said to be very harmful to the catalyst, but ferrous oxide does not show this effect.[151]

Formation of dimethyl ether on a zinc chromate catalyst was shown by Brown and Galloway[152] to increase with temperature to 397° C and to be favored by low space velocity.

Frolich and coworkers[153] have studied zinc-oxide-copper catalysts in synthesis and decomposition of methanol and concluded that maximum decomposition occurs when zinc oxide is present in excess. When samples of a catalyst containing 58.3 mole percent of zinc oxide and 41.7 of cupric oxide were reduced[154] at progressively higher temperatures, it was found that, in the decomposition of methanol, the activity of the catalysts increased slowly with the temperature of reduction to a certain point and then fell very rapidly. These catalysts were found to be crystalline for all temperatures of reduction. Catalysts containing copper and zinc in various proportions[155] were made by coprecipitation of the hydrates, dehydration of the gel, and reduction with methanol vapor at 200 to 220° C, then examined by X-rays. Every composition was found to be decidedly crystalline, possessing the characteristic crystal structure of the two components, copper and zinc oxide, but the unit cell sizes of each were markedly influenced by the size of the other.

Zolotov and Shapiro[156] found that the zinc oxide-cupric oxide catalyst undergoes reduction at not less than 220° C, the cupric oxide being completely and the zinc oxide partly reduced. It was found that α-brass was formed and its zinc content increased with duration of contact with methanol.

Kostelitz and Hüttig[157] studied the system of zinc oxide-cupric oxide as a methanol decomposition catalyst and concluded that any combination of the oxides was more active than either pure oxide. Increased pressure in preparing catalyst pellets improved the selectivity of the catalyst for decomposition of methanol into hydrogen and carbon monoxide and also improved the mechanical properties of the catalyst.

Several patents covering use of zinc oxide with copper or copper oxides have been granted.[158] Use of alloys of copper and zinc containing some partly reduced oxides of the alloy has been patented by Gabriel

150 Dolgov, B. N., and Karpinskiĭ, M. N., *Khim. Tverdogo Topliva*, **3**, 406–18, 559–68 (1932).

151 Ivanov, K. N., Kozlov, L. I., and Sofer, M. A., *J. Chem. Ind. (U.S.S.R)*, **13**, 406–8 (1936).

152 Brown, R. L., and Galloway, A. E., *Ind. Eng. Chem.*, **21**, 310–3 (1929).

153 Frolich, P. K., Fenske, M. R., and Quiggle, D., *Ind. Eng. Chem.*, **20**, 694–8 (1928).

154 Nussbaum, R., Jr., and Frolich, P. K., *ibid.*, **23**, 1386–9 (1931).

155 Frolich, P. K., Davidson, R. L., and Fenske, M. R., *ibid.*, **21**, 109–11 (1929).

156 Zolotov, N. N., and Shapiro, M. I., *J. Gen. Chem. (U.S.S.R.)*, **4**, 679–82 (1934).

157 Kostelitz, O., and Hüttig, G. F., *Kolloid-Z.*, **67**, 265–77 (1934).

158 Woodruff, J. C., and Bloomfield, G., Brit. Pats. 271,840, 279,378 (1926); U. S. Pat. 1,625,-924 (1927). Commercial Solvents Corp., Fr. Pat. 635,023 (1927).

and Brown.[159] Schmidt and Ufer [160] have claimed production of methanol and other organic compounds by passage of an oxide of carbon and hydrogen over a catalyst containing copper 10 parts and zinc 1 part. Dodge [161] has patented a highly active catalyst prepared by reducing copper carbonate admixed with zinc carbonate in the proportions of at least 2 atoms of zinc to 1 atom of copper.

Catalysts containing copper, zinc oxide, and chromic oxide have been extensively studied in Russia, and Pospekhov [162] has reviewed the literature and patents dealing with the use of these catalysts in synthesis of methanol. Dolgov [163] reported that $Cu_{49}Zn_{43}Cr_8$ and $Cu_{50}Zn_{40}Bi_{10}$ gave 86 and 75 percent conversion of carbon monoxide to methanol respectively at 360 and 400° C. Plotnikov and Ivanov [164] reported that for 91 copper, 8 zinc oxide, 1 chromic oxide, prepared by precipitation of hydroxides from a mixed solution of the salts followed by reduction, gave a catalyst that was active at 250° C and converted as much as 70 percent of the carbon monoxide to condensate which contained about 85 percent methanol. It has been claimed that, with 60 to 70 percent copper and zinc oxide to chromic oxide in the ratio 8 : 1, highest conversion of carbon monoxide into combustible liquids was obtained but that the quality of the products was highest at 55 percent copper.[165] Catalysts containing

60 copper, 35.6 zinc oxide, 4.4 chromic oxide, and 16 zinc-chromic oxide, 82 copper with 0.15 mole percent of potassium hydroxide showed activity at 200° C and 100 atmospheres and gave principally methanol and ethanol. At higher space velocities the formation of ethanol was favored.[166] The addition of powdered copper to the second of the catalysts above decreased its activity but improved methanol formation. If cupric oxide was added, its activity was not changed, but formation of higher alcohols was increased.[167] A copper oxide-zinc oxide-chromic oxide catalyst, in the proportions 9 : 15 : 7, has been patented by Karpov.[168]

Fenske and Frolich [169] found that a catalyst composed of the oxides of copper, zinc, and chromium in the molal ratio 49 : 43 : 8 had considerably higher activity for both the decomposition and the synthesis of methanol than any of the binary systems copper-zinc or chromium-zinc discussed in earlier papers of Frolich and coworkers. The catalyst at temperatures above 250° C decomposed methanol almost entirely into carbon monoxide and hydrogen (33 and 67 percent). In synthesis, the catalyst was found to be active at low temperatures and to give high conversions to methanol. A catalyst comprising an intimate mixture of zinc and chromic oxides and finely divided free copper has been patented by Dodge.[170] A zinc oxide-chromic oxide-copper oxide mixture containing about 13 per-

159 Gabriel, C. L., and Brown, B. K., Can. Pat. 271,569 (1927) ; U. S. Pat. 1,875,722 (1932).

160 Schmidt, O., and Ufer, J., U. S. Pat. 1,-818,165 (1931).

161 Dodge, B. F., U. S. Pat. 1,908,696 (1933).

162 Pospekhov, D. A., Mem. Inst. Chem. Ukrain. Acad. Sci., 5, 507–15 (1938).

163 Dolgov, B. N., Khim. Tverdogo Topliva, 3, 185–204 (1932).

164 Plotnikov, V. A., and Ivanov, K. N., J. Chem. Ind. (U.S.S.R.), 7, 1136–45 (1930) ; J. Gen. Chem. (U.S.S.R.), 1, 826–44 (1931).

165 Plotnikov, V. A., Ivanov, K. N., and Pos-

pekhov, D. A., J. Chem. Ind. (U.S.S.R.), 8, 119–26, 472–8 (1931).

166 Pospekhov, D. A., and Shokol, A. A., Mem. Inst. Chem. Ukrain. Acad. Sci., 4, 205–12 (1937).

167 Pospekhov, D. A., J. Chem. Ind. (U.S.S.R.), 14, 173–6 (1937).

168 Karpov, A. Z., Russ. Pat. 47,687 (1936).

169 Fenske, M. R., and Frolich, P. K., Ind. Eng. Chem., 21, 1052–5 (1929).

170 Dodge, B. F., U. S. Pat. 2,014,883 (1935).

cent FeCr has been patented by Eversole.[171]

Smith and Hawk,[172] using the decomposition method, concluded that mixtures of the oxides of zinc and uranium and of zinc and vanadium would probably be good methanol-synthesis catalysts. A variety of other combinations of zinc with oxides or halides of other metals have been patented. Among these may be mentioned zinc oxide, 3 moles, bismuth trioxide, 1 mole;[173] zinc oxide with about 10 percent ferric hydroxide;[174] and at least 2 mole proportions of zinc oxide with acidic oxides of metals such as basic chromates, vanadates, tungstates, and manganates.[175] Woodruff and Bloomfield[176] have patented the use of zinc oxide, chromic oxide, or other difficultly reducible metal oxides with easily reducible oxides such as those of copper, silver, iron, nickel, or cobalt and with zinc chloride, magnesium bromide, or other metallic halides. Mittasch, Pier, and Winkler[177] have patented the use of mixtures of at least two oxides (nonreducible to metals under the conditions of the process) of metals belonging to different periodic groups such as zinc and chromium, zinc and uranium, zinc and vanadium, zinc and tungsten, magnesium and molybdenum, or cerium and manganese, the more basic oxide being used in larger proportion. One of the earlier Badische[178] patents covered use of zinc oxide with an oxide of chromium, vanadium, uranium, and tungsten, and methanol catalysts prepared by igniting basic zinc carbonate or zinc and chromium carbonates have been patented.[179] In contrast to the claims in the Mittasch, Pier, and Winkler patent[177] mentioned, Badische Anilin und Soda Fabrik[180] has claimed methanol catalysts comprising a mixture of two or more metals whose oxides can be reduced to metal by hydrogen or carbon monoxide at ordinary pressures and a temperature below 500° C. Suitable metals were copper, silver, lead, zinc, and cadmium.

A series of chromium catalysts for methanol synthesis have been covered in several patents by Lazier.[181] These catalysts are prepared by igniting a metallic chromate or dichromate at 600 to 1,000° C, by prolonged heating to redness of mixtures of metallic oxides or salts with alkali chromates or dichromates, or by igniting at redness a double chromate or dichromate of a metal with ammonia or an organic base. Chromites thus prepared of zinc, copper, cadmium, magnesius, manganese, silver, or iron, or their mixtures, were claimed to be suitable methanol catalysts. A chromium-manganese catalyst has been made by decomposing a mixture of chromium and manganese carbonates.[182]

171 Eversole, J. F., Can. Pat. 359,414 (1936).
172 Smith, D. F., and Hawk, C. O., *J. Phys. Chem.*, **32**, 415–24 (1928).
173 Henry, C., Fr. Pat. 651,194 (1926). Soc. française de catalyse généralisée, Brit. Pat. 265,-984 (1926). Lefort, T. T., Can. Pat. 276,300 (1927).
174 Woodruff, J. C., and Bloomfield, G., U. S. Pat. 1,608,643 (1926) ; Can. Pat. 274,912 (1927).
175 Patart, G., Brit. Pat. 252,361 (1925).
176 Woodruff, J. C., and Bloomfield, G., Brit. Pats. 271,840, 279,378 (1926) ; U. S. Pats. 1,-625,924–8 (1927). Commercial Solvents Corp., Fr. Pat. 635,023 (1927).
177 Mittasch, A., Pier, M., and Winkler, K., U. S. Pat. 1,558,559 (1925).

178 Badische Anilin und Soda Fabrik, Brit. Pat. 227,147 (1923).
179 Smith, H. G., Franklin, R. G., and Imperial Chemical Industries, Ltd., Brit. Pat. 316,-113 (1928).
180 Badische Anilin und Soda Fabrik, Brit. Pat. 237,030 (1924).
181 Lazier, W. A., Brit. Pat. 272,555 (1926) ; U. S. Pats. 1,746,781–3 (1930), 1,829,046 (1931) ; Can. Pat. 315,876 (1931).
182 Smith, H. G., Franklin, R. G., and Imperial Chemical Industries, Ltd., Brit. Pat. 316,-113 (1928).

Larson [183] has prepared a chromium-base catalyst by mixing chromic acid with a soluble hydroxide and a salt of a heavy metal whose hydroxide is oxidizable by sexivalent chromium, such as ferrous sulfate.

Brown and Galloway [184] have studied methanol and dimethyl ether formation on a catalyst containing 3 atoms of copper to 1 of chromium, and found methanol to be produced in higher proportion below 300° C.

Kostelitz [185] has reported the preparation of a series of cupric oxide-chromic oxide catalysts and studied decomposition of methanol in them at 300, 320, and 360° C.

It has been claimed [186] that oxides of carbon can be hydrogenated at ordinary or slightly raised pressure and at relatively low temperatures, suitably 100 to 250° C, by means of catalysts comprising copper and one or more oxides of a metal of groups II to VII, but according to Larson the equilibrium amount of methanol at atmospheric pressure and 200° is 0.3 percent, which is too low to make operation practical commercially. Larson further doubted that any catalysts are active enough to give approach to equilibrium at reasonable space velocity of gas at temperatures as low as 200° C. Catalysts comprising a mixture of an element of the first subgroup of the periodic system and a large quantity of an element of the eighth group preferably from the iron group) have been patented [187] for use in preparing organic compounds, and a re-duced copper-nickel catalyst has been patented for use in making gaseous mixtures of carbon monoxide and hydrogen by decomposition of methanol.[188]

Fused mixtures of copper oxide and an oxide of manganese, tungsten, zinc, cadmium, molybdenum, or titanium, and fused mixtures of copper and manganese oxides together with oxides of the other metals listed above have been patented by Larson [189] as methanol catalysts.

A catalyst containing copper and one or more of the elements titanium, vanadium, chromium, or manganese, or brass, but free from iron or nickel, has been claimed [190] to be active at 200° C, but this claim seems doubtful in view of Larson's experience, quoted above.

Another patent [191] claims that an intimate mixture of at least two oxides of the third and fourth groups in which the oxides of acid character preponderate over those of more basic character may be used in addition to ordinary catalysts to reduce formation of secondary products. In an example the catalysts contain copper 60, manganese dioxide 55, cerite 55, and silica 240 parts.

Schmidt and Ufer [192] have patented catalysts consisting of compounds of titanium or metals of the fourth group of the periodic table with added activators.

Mittasch and Pier in 1926 patented the use of oxides of vanadium, uranium, and aluminum or of metals such as copper, silver, lead, or zinc when promoted by metal oxides or salts of the fourth to seventh group of the periodic system.

[183] Larson, A. T., U. S. Pat. 1,908,484 (1933).
[184] Brown, R. L., and Galloway, A. E., *Ind. Eng. Chem.*, **22**, 175–6 (1930).
[185] Kostelitz, O., *Kolloid-Beihefte*, **41**, 58–72 (1934).
[186] I. G. Farbenindustrie A.-G., Brit. Pat. 308,181 (1927).
[187] I. G. Farbenindustrie A.-G., Brit. Pat. 317,-808 (1928).

[188] Eversole, J. F., U. S. Pat. 2,010,427 (1935)
[189] Larson, A. T., Can. Pat. 307,671 (1931); U. S. Pats. 1,844,129, 1,844,857 (1932), 1,939,-708 (1933), 2,061,470 (1936).
[190] Schmidt, O., and Ufer, J., Can. Pat. 251,-486 (1925).
[191] DeLacotte, A. H., Fr. Pat. 835,899 (1939).
[192] Schmidt, O., and Ufer, H., Ger. Pat. 608,-361 (1935).

Smith and Hawk [198] found cadmium oxide and chromic oxide was a good methanol decomposition catalyst.

A few catalysts contain magnesium as a principal or important ingredient.[194] It is claimed to confer high mechanical stability, especially on catalysts of the metal oxide type, and amounts to about 90 percent of a catalyst patented by Woodruff and Bloomfield.[195]

Complete absence of iron in the methanol catalyst or catalyst container was stated to be necessary in early patents,[196] but a few patents [197] covering the use of the iron group compounds with oxides of other elements, such as chromium, vanadium, tungsten, zirconium, aluminum, titanium, manganese, and zinc, have been granted; however, it is said that the presence of metallic iron, cobalt, or nickel must be avoided. In contrast to the previous claim that metallic nickel must be avoided, nickel in the amount of 2 to 10 percent as metal or oxide added to irreducible oxides has been patented [198] for production of methanol from a mixture containing carbon monoxide, hydrogen, nitrogen, and methane at 800 atmospheres pressure and 300° C, and reducible nickel compounds, such as hydroxide, oxide, nitrate, oxalate, or tartrates, are formed into tablets, then suitably reduced and used as methanol catalysts.[199]

A catalyst containing cobalt with zinc and chromium oxides or zinc and manganese oxides or a mixture of all these oxides is also covered in the patent of Morgan and Taylor.[197]

An early patent [200] claiming catalytic production of formaldehyde or methanol by hydrogenation of carbon monoxide or carbon dioxide with platinum or nickel catalysts has not been successfully applied.

Lead and strontium oxides in the atom proportions of 1 to 3 or 4 have been patented [201] as methanol catalysts.

Tropsch and Schellenberg [202] had to use temperatures in the neighborhood of 500° C to decompose methanol on iron, tinned iron, or aluminum. Products of decomposition were carbon, carbon dioxide, and methane, in addition to carbon monoxide and hydrogen.

Soluble salts of uranium, tungsten, vanadium, zinc, beryllium, chromium, or titanium have been deposited on a porous support, such as pumice, asbestos, charcoal, or activated carbon,[203] to give a methanol catalyst.

Decomposition of methanol on platinum metals has been studied by Hüttig and Weissberger,[204] and production of a gas containing 2 parts hydrogen and 1 part carbon monoxide was found to be erratic in the early stages of use. In order of

[198] Smith, D. F., and Hawk, C. O., *J. Phys. Chem.*, **32**, 415–24 (1928).

[194] I. G. Farbenindustrie A.-G., Brit. Pat. 286,-284 (1927).

[195] Woodruff, J. C., and Bloomfield, G., U. S. Pat. 1,609,593 (1926); Can. Pat. 274,911 (1927).

[196] Badische Anilin und Soda Fabrik, Brit. Pats. 229,715 (1923), 237,030, 240,955 (1924). Mittasch, A., and Pier, M., Ger. Pat. 565,309 (1923); U. S. Pat. 1,569,775 (1926).

[197] Badische Anilin und Soda Fabrik, Brit. Pat. 254,760 (1925). Morgan, G. T., and Taylor, R., Brit. Pat., 313,061 (1928). Natta, G., and Faldini, M., Fr. Pat. 658,788 (1928). Pier, M., Wietzel, R., and Winkler, K., U. S. Pat. 1,917,323 (1933).

[198] Compagnie de Béthune, Brit. Pat. 275,600 (1926); Fr. Pat. 633,139 (1926).

[199] Woodruff, J. C., Brit. Pat. 279,377 (1926). Commercial Solvents Corp., Fr. Pat. 636,337 (1927).

[200] Dreyfus, H., Brit. Pat. 157,047 (1917).

[201] Soc. française de catalyse généralisée, Brit. Pat. 265,984 (1926). Henry, C., Fr. Pat. 651,-194 (1926).

[202] Tropsch, H., and Schellenberg, A., *Ges. Abhandl. Kenntnis Kohle*, **7**, 13–4 (1922-3).

[203] Compagnie de Béthune, Brit. Pat. 274,492 (1926); Fr. Pat. 632,259 (1926).

[204] Hüttig, G. F., and Weissberger, E., *Siebert Festschr.*, **1931**, 173–8.

decreasing activity after a steady state was reached were palladium, osmium, rhodium, ruthenium, indium, and platinum. With all these metals the activities were higher than with a zinc oxide catalyst.

Pure zinc sulfide has been reported [205] to be a methanol decomposition catalyst giving 100 percent decomposition at 300 to 375° C. By addition of 1 percent of the sulfides of cadmium, molybdenum, copper, and antimony, 100 percent decomposition was obtained at 300 to 325° C, but the percentage of carbon monoxide in the gas was lowered.

In a few patents, sulfides have been reported to be methanol-synthesis catalysts. Zinc sulfide alone or mixed with chromium oxide or other promoters has been so claimed.[206] Use of metal sulfides (except iron), especially those from the fifth and sixth groups of the periodic system, for many purposes, including methanol synthesis, has also been patented.[207] In one of the earliest methanol patents,[208] sulfides, silicides, borides, phosphides, and arsenides of chromium, vanadium, tungsten, zirconium, aluminum, and titanium were mentioned as addition agents for catalysts made of iron, cobalt, or nickel oxides.

Porous carbon, preferably from wood charcoal, has been patented as a methanol catalyst by Grenier.[209] Wood charcoal or active carbon as an addition to catalysts consisting of formates of zinc or chromium has also been patented.[210]

Halides have been mentioned as components of methanol catalysts in numerous patents,[211] but the advantages conferred by the halides have not been disclosed.

Alcoholates, such as those of sodium and cadmium, have been patented [212] for synthesis of methyl formate and methanol.

Some of the early patents [213] covered a great number of possible methanol catalysts. Among the general classes of material were metal oxides or compounds which are not reduced by the reaction gases at temperatures up to 550° C under pressure, but nickel, iron, and cobalt had to be excluded from the catalyst materials

Mittasch, Pier, and Müller [214] patented methanol catalysts consisting of metal oxides not reduced to metals under the conditions of the reaction (450° C and 200 atmospheres pressure), such as oxides of alkali, alkaline earth, or earth metals containing no iron, nickel, or cobalt. Mixtures have also been patented [215] containing compounds of potassium, rubidium, or cesium and readily reducible metal oxides or reduction products, such as copper, silver, gold, tin, lead, bismuth, cadmium, thallium, and metals of the platinum groups, but iron, nickel, and cobalt must be avoided.

Catalysts consisting of mixtures of oxides of metals of different groups in copper apparatus in the absence of iron, nickel, and

205 Dolgov, B. N., Karpinskii, M N., and Silina, N. P., *Khim. Tverdogo Topliva*, 5, 470–4 (1934).

206 British Celanese, Ltd., Bader, W., and Thomas, E. B., Brit. Pat. 334,924 (1929).

207 I. G. Farbenindustrie A.-G., Brit. Pat. 379,335 (1932).

208 Badische Anilin und Soda Fabrik, Brit. Pat. 254,760 (1925).

209 Grenier, R. J. A., Brit. Pat. 271,523 (1926).

210 Compagnie de Béthune, Ger. Pat. 534,551 (1927).

211 Woodruff, J. C., and Bloomfield, G., Brit. Pat. 272,864 (1926); Can. Pat. 274,915 (1927). Commercial Solvents Corp., Fr. Pats. 34,861, 644,525 (1927). Woodruff, J. C., Bloomfield, G., and Bannister, W. J., U. S. Pat. 1,695,447 (1928).

212 Scott, N. D., U. S. Pat. 1,946,245 (1934).

213 Badische Anilin und Soda Fabrik, Brit. Pat. 229,714 (1923).

214 Mittasch, A., Pier, M., and Müller, C., Ger. Pat. 544,665 (1923).

215 Mittasch, A., and Pier, M., Ger. Pats. 628,-427, 636,682 (1936).

cobalt have been patented,[216] examples being zinc oxide with oxides of chromium, uranium, vanadium, or tungsten, magnesium and molybdenum oxides, cerium and manganese oxides, and cadmium and chromium oxides.

Potash-lime and potash-alumina catalysts have also been mentioned by Mittasch, Pier, and Müller.[217] A whole range of hydrocarbons and their oxygenated derivatives, including methanol, was prepared on a catalyst consisting wholly or mainly of a sintered metal of the iron group, to which was added an alkali compound, such as halide or phosphate. Other activating substances added in minor proportions were alumina, silica, compounds of copper, titanium, manganese, tungsten, molybdenum, chromium, thorium, cerium, and zirconium or other rare-earth metals.[218]

Coal tars, mineral oils, resins, and similar materials have been treated with a mixture of hydrogen and carbon monoxide under high temperature and pressure in the presence of methanol catalysts, either alone or with molybdenum, tungsten, or chromium to give organic products among which are methanol and benzene.[219] Use of elements of the chromium or boron groups as methanol catalysts was patented in 1923.[220]

The Standard Oil Development Company[221] has patented the preparation of active catalysts of high mechanical strength that may be used for many purposes, including synthesis of methanol, by mixing an effective catalytic substance, which is preferably present in minor proportion with at least two other substances, one as a major and the other as a minor constituent, capable of reacting with each other to the exclusion of the effective catalyst to form a compound or solid solution having a melting point substantially higher than the reaction temperature, and then heating the mixture to a temperature of 1,600° F or higher for a time insufficient to cause substantial melting. A similar type of catalyst has been patented by the International Hydrogenation Patents Company.[222]

A few general methods of catalyst preparation have been patented,[223] among them the preparation of balls of oxide catalyst by heating metal carbonates, and the distribution of the catalyst throughout a coke by mixing the catalytic substances in a coal-oil mixture and coking it.[224]

Spent methanol catalysts such as oxides or oxides mixed with metals may be reactivated by the action of hydrogen on them at higher temperatures but at similar pressures.[225]

Essentially the same mixture of hydrogen and carbon monoxide can be used to synthesize higher alcohols and other oxygenated derivatives by changes in catalysts, temperature, or relative proportions of carbon monoxide and hydrogen. Wietzel and Luther[226] used a catalyst containing alkalies and hydrogenating and dehydrogenating constituents in suitable proportions; for example, one part each of potassium car-

[216] Badische Anilin und Soda Fabrik, Brit. Pat. 227,147 (1923).

[217] Mittasch, A., Pier, M., and Müller, C., U. S. Pat. 1,791,568 (1931).

[218] I. G. Farbenindustrie A.-G., Brit. Pat. 506,064 (1939).

[219] Krauch, C., and Pier, M., Ger. Pat. 671,606 (1939).

[220] Ufer, H., and Schmidt, O., Ger. Pat. 565,880 (1923).

[221] Standard Oil Development Co., Brit. Pat. 485,178 (1938).

[222] International Hydrogenation Patents Co., Ltd., Fr. Pat. 818,078 (1937).

[223] Imperial Chemical Industries, Ltd., Fr. Pat. 672,797 (1929).

[224] Stephenson, H. P., Brit. Pat. 449,603 (1936).

[225] British Celanese, Ltd., Bader, W., and Thomas, E. B., Brit. Pat. 334,251 (1929).

[226] Wietzel, R., and Luther, M., Ger. Pats. 625,757, 628,557 (1936).

bonate, vanadium trioxide, and cupric oxide. In an addition to the patent, they mentioned a greater amount of hydrating than hydrogenating catalyst and also mentioned use of a lower temperature for higher alcohol and other oxygenated compound formation. Cadmium chromate was mentioned as a suitable catalyst. Morgan, Hardy, and Proctor [227] claimed higher yields of higher alcohols when the catalysts were precipitated by alkali hydroxides than when formed by ignition of nitrates. Their highest yield was given by a catalyst impregnated with 9.8 percent of rubidium. Bocharova, Dolgov, and Petrova [228] ob-

tained increased yields of higher alcohols by means of a more alkaline catalyst. Berl and Bemmann [229] found that zinc oxide containing alkali gave higher alcohols, acids, and aldehydes in contrast to principally methanol from alkali-free zinc oxide.

It has been clearly demonstrated in the laboratories of the British Chemistry Research Board [230] that extremely high pressure (2,500 atmospheres) does not influence the characteristics of the product from a copper-chromite methanol catalyst at 240° C. The products were iron carbonyl and methyl alcohol, the alcohol distilling from 64.7 to 64.9° C.

[227] Morgan, G. T., Hardy, D. V. N., and Proctor, R. A., *J. Soc. Chem. Ind.*, **51**, 1-7T (1932).

[228] Bocharova, E. M., Dolgov, B. N., and Petrova, Yu. N., *J. Chem. Ind. (U.S.S.R.)*, **12**, 1249–55 (1935).

[229] Berl, E., and Bemmann, R., *Z. angew. Chem.*, **44**, 34–9 (1931).

[230] *Dept. Sci. Ind. Research (Brit.), Chem. Research Board, Rept. for the Triennial Period Ending December 31, 1937*, p. 33.

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